

CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, O.B.E., D.Sc., F.I.C.

No. VI

The Chemistry of Coal

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THE progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

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THE CHEMISTRY OF COAL

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PREFACE

THE literature dealing with coal and its chemical properties is of such an extent that an exhaustive record of the facts and theories contained therein would occupy volumes. All that is attempted in this monograph is to show the chief methods by which the problems of coal-constitution have been attacked, and to outline some of the more interesting results obtained. It is hoped in this way to indicate to those desirous of carrying out research work on coal and kindred substances lines along which investigation may lead to concrete conclusions. An attempt has been made to mention all the more important papers in the bibliography, as it was felt that to anyone contemplating serious research work on coals this section should be of value.

The methods described in the section on analysis are those which I have found in practice to be satisfactory, and I hope that this section will prove of value to those who have occasion to examine coals from the analyst's point of view.

J. B. R.

June 1919.

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THE CHEMISTRY OF COAL

I.

CLASSIFICATION AND OCCURRENCE OF COAL.

What is Coal?—This question has interested and perplexed both the geologist and the chemist as they have searched for its ultimate origin and composition. For, although coal in all its varieties is of such common occurrence and of such economic importance, yet the history of its formation and the secrets of its structure still furnish subjects for research in geology and chemistry. These questions are far from being finally solved, but during the last ten or twenty years many interesting advances have been made in the chemistry of coal and allied substances, and the literature on the subject is now of considerable magnitude. As illustrating the lack of knowledge as regards coal which existed in the middle of last century, the Torbanehill dispute may be instanced. In 1850 the coal on the estate of Torbanehill, near Bathgate, was let by the proprietors to a firm of coalmasters. Two years later it was found that the lessees were raising and selling as a gas-coal the mineral now known as Torbanite or Boghead coal, and their right to do so was challenged. A lengthy

litigation followed as to whether this substance was a "gas- or cannel-coal" or a "bituminous shale," and seventy-six scientists were called as witnesses. Judgment was finally given for the lessees on the ground that the substance was "coal" in the popular or commercial sense of the term. An appeal was made to the House of Lords, and ultimately the matter was compromised.¹ The question of the nature of "Boghead" coal is still a matter of discussion.

Classification of Coals.—Before proceeding to discuss the chemical nature of coal, it is necessary to say a little on the classification of coal species and on the suggested theories of their origin.

The different varieties of coal grade into each other, so that a rigid separation into classes is impossible, but, in general, a coal may be placed in one or other of the following five divisions.

1. *Lignites or Brown Coals.*—These are all of geologically recent origin, and are probably a stage in the series of changes by which wood and other vegetable matters are gradually converted into true coal. In most lignites the texture of the parent substance is still well-defined. "Brown Coal" is a name often used distinct from lignites to signify a coal of older geological age which has become more compacted and has lost most of the evident vegetable structure. Lignites and brown coals are of rare occurrence in Britain, but are of importance on the Continent, in the Western United States, and in Australia.

2. *Cannel Coals* exhibit few traces of vegetable structure, are black or brown in colour, burn with

a bright, candle-like flame (hence the name), and have a conchoidal fracture. They are of importance in gas-making.

3. *Bogheads or Torbanites* are somewhat similar to cannel coals, but have a much higher percentage of ash, and resemble the oil-shales in the percentage of volatile hydrocarbons evolved on destructive distillation. They are of rather limited occurrence, being found at Torbanehill and Boghead in Scotland, in Central France, in New South Wales, and in a few other localities.

4. *Bituminous or Humic Coals* are very variable in character. They are the ordinary household coals. They burn with a smoky flame, but contain no "bitumen" as such, hence the alternative name is preferred by many writers. They have a rectangular, rather than a conchoidal, fracture, and can in this way be easily distinguished from the cannel coals.

5. *Anthracites*.—These are black or brown, and often have a shining lustre. They are hard—and break with conchoidal fracture. Analysis shows little hydrogen, oxygen, or nitrogen present, and the volatile matter is small in amount. Anthracites are thus difficult to ignite, but give more heat per unit than any other coal.

Classification by Analysis.—Many different schemes based on analytical results have been suggested. One of the best of these is that of Seyler,² who forms genera according to the hydrogen percentage and species according to the carbon percentage. Another method of classification is

based on the carbon-hydrogen (C/H) ratio. Various limits for the different varieties of coal have been given by different analysts. The United States Geological Survey has finally adopted the following limits:—

		C/H ratio.		
Graphite	∞	to	?
Anthracite	?	„	26
Semi-anthracite	26	„	23
Semi-bituminous	23	„	20
Bituminous	20	„	11.2
Lignite	11.2	„	9.3
Peat	9.3	„	?

According to Seyler's scheme the following limits are obtained:³—

		C/H ratio.		
Anthracitic genus	18.75	and over	
Carbonaceous genus	16.6	to 24	
Semi-bituminous genus	15.0	„ 21.2	
Bituminous genus	12.9	„ 19.0	
Per-bituminous genus	13.8	and less to 16.2	

It will be seen from these figures that a rigid separation of coals into distinct classes is quite impossible, but, at the same time, a working basis of classification is possible and desirable.

The Occurrence of Coal.—Coal is widely distributed throughout the world, and occurs in the stratified rocks of most of the geological epochs from the pre-Cambrian to the Miocene, and, if we accept peat as a form of coal, to the strata being laid down at the present day.

The oldest coals⁴ are found in Devonian rocks in the polar regions, and are of the bituminous or

humic variety. Graphites, which are possibly derived from vegetable matter as the ultimate result of coal metamorphism, occur in the still older rocks of the pre-Cambrian series in Canada.

The Carboniferous strata are particularly rich in coal beds. These occur in Scotland, England, Wales, France, Germany, India, Australia, South Africa, the United States, Brazil, Chili, the Argentine, and other countries.

Permian coals are important in Central France, Saxony, and Bohemia; Triassic coals in Japan; and Jurassic coals occur in different parts of Britain, Hungary, Russia, and Japan.

Cretaceous strata in the Rocky Mountains region and in Alaska contain coal of the lignite variety.

Tertiary deposits of lignites or brown coals are present in the United States, Germany, Hungary, Russia, and Japan, and at Bovey Tracey in Devonshire.

So many industries are dependent on coal as a source of energy and upon its by-products as raw materials in important manufactures, that the prosperity or otherwise of many countries is conditioned largely by the presence or absence of easily attainable and workable coal supplies of good quality. Although coal is so widely distributed, and coal deposits extend to large areas, yet the world's usage of coal, if continued at the present rate, must within a calculable period of time lead to exhaustion of the easily available supplies, and already many schemes for its conservation and the ensuring of its being used to the maximum advantage have been formulated.

II.

THE ORIGIN OF COAL.

Geological Theories of the Origin of Coal.—The existence of gradations between the different varieties or classes of coal would suggest that coal strata have been formed in essentially one manner, but that there have been certain minor conditioning factors which have caused variation towards anthracites at one end of the series or towards lignites at the other. The theories offered to account for coal formation are very numerous, and much writing has taken place on the subject. The view that coals have resulted from eruptions of bitumen has been several times advanced in the past, but to-day has very few supporters in comparison with the theories of origin from living organisms, and it is generally agreed that all coals, with a possible few exceptions where they are derived from animal remains, have resulted from vegetable deposits. This view is supported by the frequent impressions of plant remains found in coals, and also by microscopic examination. Thus, well-defined plant fossils such as *Sigillaria* and *Stigmaria* have been noted by all who have even casually examined certain coals. In torbanites, again, there occur peculiar small, round, orange-yellow bodies which, on microscopic examination, have been

variously classed as gelatinous algae,⁵ the megaspores of vascular cryptogams,⁶ or as merely resinous concretions.⁷ Recently, much microscopic work has been done on coals with a view to determining their properties as conditioned by their structure, and Lomax⁸ suggests microscopic examination as a guide to the relative inflammability of the dust. He states that the organic matter in coals may be classed as droppings of trees or other plants in the shape of spores, fruits, leaves, twigs, fragments of stems, etc., mingled with resinous matter, and that the inflammability of the dust is mainly conditioned by the extent of the last-named constituent. Hickling⁹ gives a detailed catalogue of the constituents of coal which may be summarised as—(1) “lignitoid” tissue, *i.e.*, plant fragments which have been impregnated with liquid decomposition products of other plants; (2) glossy cuticles from stems or leaves; (3) hard coats of spores; (4) dark-coloured matrix of comminuted debris; (5) resin globules and strands; (6) lignified tissue resembling charred wood; and (7) the gelatinous “algæ” of Bertrand and Renault. He classifies coals as “humic,” “canneloid,” or “boghead,” according as lignitoid material, spores and comminuted matrix, or “algæ” predominate.

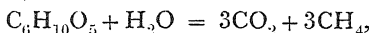
If such substances, then, are the mother materials of coal, the question immediately presents itself—How have these vegetable materials become so altered in properties during their change into coal? It must be remembered that the time factor is of great importance in this connection, and that reactions which are so slow as to be impossible of demonstra-

tion in the laboratory may quite easily be carried to completion during the lapse of the millions of years which go to make up geological ages. Temperature and pressure are other factors whose importance it is difficult to gauge exactly.

The Peat-to-Anthracite Theory is that peat has been converted into brown coal, the brown coal into humic or bituminous coal, and this finally into anthracite, pressure and temperature being the main agents in the transformation. Hoffmann¹⁰ opposes to this view the very pertinent question, Why then does not anthracite contain more ash than peat? Donath,¹¹ from the results of experiments on coals, concludes that lignites and anthracites, at least in the greater number of their types, are entirely distinct in origin, and that lignites cannot be altered into anthracites. He states that the vegetable material which produced lignite contained much lignin, whereas that responsible for anthracite was rich in protein substances (which may have been animal in origin) and very poor in lignin, and that in the formation of anthracite a more or less far-reaching destructive distillation with polymerisation or condensation of the products has in general taken place.

The Peat-to-Anthracite theory is now accepted by few authorities, its place being taken by what is known as the **Metamorphic Theory**. This states that the vegetable material from which the coal is formed underwent two series of changes, the first being a fairly rapid alteration due to the action of bacteria, and the second a much slower form of

modification which took place after stratification, when the material was subjected to pressure due to earth movements and somewhat comparable with the change of limestone into marble.¹² Renault¹³ claimed actually to have observed certain petrified micrococci in some coals he examined. Cellulose¹⁴ is decomposed by amylo-bacterium in accordance with the equation—



and carbon dioxide and methane are very abundant in coal-mines. By digging down into a peat-bog one can frequently observe under the recent moss and above the more compacted material which forms true peat, a layer of dark, gelatinous, waterlogged material, which is, in all likelihood, the final product of bacterial action. Smythe¹⁵ investigated some such substance found in sandy clay underlying peat in a pitfall at Tantobie, County Durham. He found it to consist of 76 per cent. water and a residue giving on analysis—

C, 49.29 per cent.; H, 5.15 per cent.; N, 2.41 per cent.;
S, 1.41 „ O, 30.51 „, and Ash, 11.23 „

On such decomposed material the metamorphic theory demands the combined action of heat and pressure as the means of change into coal. As regards temperature, it is improbable that any coals have been as hot as 300° C., as at this temperature all the constituents of coal-tar distillation begin to appear, and these compounds are not normally present in coal.¹⁶ The tendency is to ascribe the greater part in the transformation to pressure.

Artificial Coal Formation.—Various experimenters have studied the effects of bacterial action, heat, and pressure on vegetable substances.

Mitscherlich carried out extensive studies on the fermentation of cellulose. He found that slices of potato placed in water under favourable conditions of temperature, etc., undergo decomposition, the cellulose diminishing, but the starch granules remaining intact. New slices placed in the filtrate underwent a more rapid decomposition than the first. The liquid was found to contain no fungi, but a large number of bacteria were present, and these Mitscherlich considered the probable cause of the phenomenon.

Van Thieghem¹⁷ studied this decomposition, and named the micro-organism responsible for it *Bacillus amylobacter*. He further showed that it was very likely that this bacillus existed in the carboniferous era. By examining thin slices of coal under the microscope he recognised cell walls which had been silicified, and thus retained evidence of the changes undergone by bacterial action, and even in some cases was able to detect the silicified remains of the bacillus itself.

Boudouard¹⁸ allowed fermentation to take place in a turf by reason of the micro-organisms contained, assisting it by application of heat and added oxygen. Humic acid was continuously formed with corresponding increase in carbon percentage. By means of pressure and heat combined he succeeded in altering this material into substances resembling bituminous coal and anthracite.

Göppert¹⁹ obtained a substance of similar appearance to lignite by heating different parts of plants with water in closed vessels to 60°-80° C. for five months, but proceeded no further with the research. This, however, showed that coal, or at least substances resembling coal, can be produced from organic materials at quite low temperatures, an important point when it is considered that many of the characteristics of coal point to its never having been subjected to anything but a very moderate temperature.

Fremy²⁰ carried out an interesting series of researches. He found that if he heated cellulose or vasculose in closed tubes for long periods of time at temperatures between 200° and 300° C., water, acids, gas, and tar were evolved, but the product, although black and brittle, still retained its original structure, and in no way resembled coal. Using, however, sugars, starches, gums, chlorophyll, fats, and resins obtained from plants, he obtained substances more nearly resembling coal. They were black, brittle, often fusible, and absolutely insoluble in neutral, acid, or alkaline solvents, and on heating evolved water, gas, and tar, and left a hard, shining coke. Still more interesting were his results with "ulmic" acid, a black and shining substance found in fossil woods and coming from the transformation of the vasculose. By heating this substance under pressure for two hundred hours he was able to produce artificial coals. He concludes, therefore, that the stages in the formation of coal have been—
(1) Formation of turf; (2) Fermentation processes,

transforming the constituents of this turf into "ulmic" acid; (3) Formation of coal from the "ulmic" acid through the agency of heat and pressure.

Thomsen²¹ experimented with a carbohydrate, isomeric with cellulose, obtained from different woods, and called by him "wood-gum," and obtained results similar to those of Fremy.

Stein,²² by heating wood in hard glass tubes in presence of superheated steam at temperatures of 245°-290° C. obtained substances containing hydrogen and carbon percentages similar to those of coal. He showed that the carbon percentage rose with increased temperature, whereas the volatile matter, chemically combined water, and the hydrogen percentages decreased.

Heuser²³ reports the formation of artificial coal in the condensing space below the perforated bottom of a wood oven. The deposit had formed during a period of six or seven years under a pressure of about five atmospheres of mingled steam and air. The substance had all the appearance of coal, but was not quite uniform. Part was brittle, porous, and of the colour of brown coal, whilst the rest resembled anthracitic coal in its hardness, colour, and density. Analyses (calculated on ash- and moisture-free material) showed the former to consist of C, 66.2 per cent.; H, 4.9 per cent.; O, 28.9 per cent., and the latter of C, 68.1 per cent.; H, 4.8 per cent.; O, 27.1 per cent. In both products there was a certain quantity of resin (6.15 per cent. in the first and 1.64 per cent. in the second). This seems to

point to the fact that the change to coal was not yet quite complete.

Boudouard²⁴ performed many experiments on the alteration of wood, turf, and brown coal by air, moisture, heat, and pressure, and the following are some of his conclusions:—(1) At 110° C., the action of air on sawdust and turf notably increases the percentage of humic acids. The percentages of carbon and volatile constituents are not sensibly changed. It is otherwise in the case of brown coal, where the humic acid almost entirely disappears, the percentage of carbon is reduced, and the volatile matter increases. (2) The percentage of carbon in the humic acid from turf is smaller than in that of bituminous coal, brown coal, or sawdust. If, however, turf is heated in presence of moist oxygen a humic acid is obtained having about 20 per cent. carbon. If still higher temperature is employed, the humic acid formed resembles that of certain bituminous coals. (3) If turf is heated in a closed tube, the humic acid contained is no longer soluble in alkali. Thus it arises that by heating natural coal in closed tubes only small traces of humic acid can be detected. In bituminous coal with a small percentage of volatile matter or in anthracite, humic acid is no longer present. Humic acid is, therefore, an intermediate product in the formation of coal.

Summary.—On the whole, the metamorphic theory seems to be a very reasonable one, but much research is still needed before its position is secure. The subject is a very complex one, and many other theories have at various times been propounded on

which it is not possible to enlarge further here. We must now proceed to investigate the chemical nature of the coal substance itself, bearing in mind as we do so these important facts already demonstrated :—

- (1) Coal is of many varieties and statements true of one kind of coal do not necessarily hold for even its near neighbour in the series.
- (2) Very varied prime materials may give rise to one and the same kind of coal, and, inversely, the same original substance may, by variation in the influences to which it has been subjected, give rise to widely different classes of final product.

III.

THE ACTION OF SOLVENTS ON COAL.

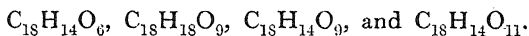
RESEARCHES into the nature of the organic matter in coals have followed three main lines, namely:— (1) Endeavours to extract constituents in an unchanged condition by means of solvents; (2) Oxidation of the coal substance by means of nitric acid and other oxidising agents; (3) Destructive distillation of the coal either under atmospheric or reduced pressure, and examination of the products. We will deal with these methods in turn.

Most of the ordinary organic solvents dissolve little, if any, material from coal. Because of the compact nature of coal, it is necessary to have it very finely powdered, and to continue the extraction for a considerable period, in order to be confident that all the matter soluble in any particular solvent has been extracted. Hence researches along this line are apt to be exceedingly prolonged and tedious. Nevertheless, much work has been done in this branch and some very important results have been obtained.

Caustic Potash extracts from coals substances of

an acid nature. Anderson and Roberts²⁵ found that for some coals treatment with caustic potash removed the coking properties (*i.e.*, the ability to form voluminous, coherent residues on ignition in a limited air supply), whilst other coals showed no change in coking properties after similar treatment. They conclude that the substances removed by the potash are of a resinous nature, and that there must be in the second type of coals another substance which is non-saponifiable, and which can induce a certain amount of coking.

Boudouard²⁶ found that coals after oxidation in air contained brown products of acid nature which dissolved in alkalis and which he classed as humic acids. He obtained them in a pure state by treating the coal with 5 per cent. caustic potash, filtering, precipitating the acid by addition of hydrochloric acid to the filtrate, washing, and drying at 110° C. Analyses of several such acids gave the empirical formulae—



He also found that only coals approaching lignites contained these acids in the natural state (1 to 5 per cent.), but that they could be detected in bituminous coals after oxidation in air at 100° C. for some time, and that similar treatment increased the content of lignites to 5 to 14 per cent. Oxidation with nitric acid increased the percentage in lignites to 8 to 50 per cent., and even developed traces in coals approaching anthracite. These acids he always

found in coals which had lost their coking powers through oxidation, and it therefore seems reasonable to conclude that the substance in the coals responsible for coking properties gives rise to these humic acids on oxidation. He ²⁷ also considered this substance to be of a cellulosic nature, as it appeared to be removed (causing disappearance of coking quality) by successive treatment of the coal with caustic potash, hydrochloric acid, and Schweitzer's reagent (ammoniacal solution of copper oxide).

Donath and Margosches ²⁸ added powdered permanganate to their alkali solvent. They heated till there was no further reduction, reduced the excess of permanganate with sodium formate, and filtered. The filtrate, after acidification with acetic acid, was treated with a solution of calcium chloride. An abundant precipitate of calcium oxalate was obtained in experiments with lignites and bituminous coals, but anthracites gave only very small precipitates. These experiments strengthen the view that lignites and bituminous coals contain a substance or substances which on oxidation give rise to acids (probably humic acids), that these on further oxidation form oxalic acid, and that these substances are absent from anthracites and non-coking coals. Alkaline hypobromite solutions have similar solvent properties.

The action of organic solvents on coals has been the basis of many experiments by different investigators. These, in general, have not shed much light on the nature of the coal substance, but some interesting results have nevertheless been obtained

especially in the case of pyridine. The literature on the subject is voluminous, but the chief results obtained may be summarised as follows.

Alcohol extracts but little from coal, the extract being usually of a yellow colour with blue fluorescence.²⁹ Reinsch³⁰ digested five hundred grams of powdered coal with one litre of 94 per cent. alcohol for three days. The solution on evaporation gave delicate, snow-white flocks like sublimed chenopodin, which the experimenter supposed to be altered chenopodin, a substance found by him in the sap of *Melilotus albus*, and to which he gave the formula $C_{12}H_{13}O_3N$.

Ether, chloroform, acetone, petroleum ether, aniline, and turpentine have extracting powers similar in degree to that of alcohol.

Acetic anhydride and glacial acetic acid have little effect.³¹

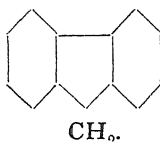
Pentane.—By means of pentane Jones and Wheeler³² obtained solid paraffins corresponding with heptacosane, $C_{27}H_{56}$, from several British coals.

Benzene.—Some interesting results have been obtained by extraction with benzene. Smith³³ extracted several coals with rectified benzene, and obtained from Boghead cannel 0.6 per cent., from Australian cannel 0.67 per cent., from American cannel 1.06 per cent., and from two Lancashire cannels 1.06 per cent. and 0.85 per cent. extracted substance respectively. From a Japanese coal having an analysis of C, 75.22; H, 5.84; N, 1.11; S, 3.15; H_2O , 0.62; he obtained as much as 9.5 per cent. extract, which was semi-fluid, tar-like, and smelled

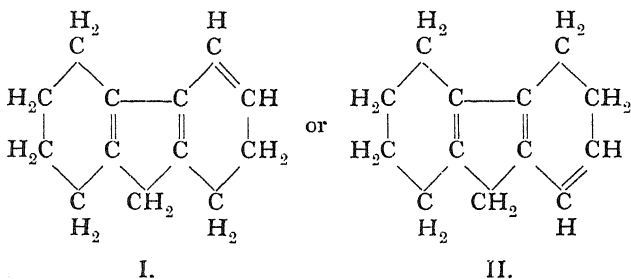
like crude petroleum. On distillation he obtained fractions which he classed as light naphtha (175° - 200°), phenols containing toluene or xylene (250° - 300°), and solid paraffins (above 300°). He considered this extract to consist of "bituminised resins" from spores, fruits, etc., of a rich vegetation.

Pictet and Ramseyer³⁴ extracted 248 kilograms of Montrambert-Loire coal in a Soxhlet apparatus with benzene. After washing the extract with caustic soda and then with sulphuric acid to remove phenols and bases, the benzene was distilled off. 244 grams of a mobile oil remained. Under 10 mms. pressure, 60 per cent. of this distilled between 110° and 265° C., the residue cooling to a dull, colophonite-like mass. It was found impossible to obtain any constant-boiling fraction from the distillate, as each fraction seemed to carry over with it some of the succeeding one. Eight fractions were ultimately made. These all consisted of substances containing no sulphur and having carbon and hydrogen percentages summing to between 93 per cent. and 99 per cent. They oxidised in air in a similar manner to the terpenes, hydrofluorenes, etc., but by distilling over sodium it was possible to raise the sum of the carbon and hydrogen percentages to almost 100. The molecular weights of fractions 1, 5, 6, 7, and 8 were found to be respectively 179, 212, 227, 256, and 296. $C_{13}H_{16}$ has a molecular weight of 172, and the authors therefore consider that fraction 1 consists of this compound, the succeeding fractions being mixtures of it with its polymers. Its density was .920 at 20° C., boiling-point 110° - 120° under 10

mms. pressure and 240° - 250° at atmospheric pressure. It decolorised bromine and permanganate solutions in the cold, and was readily attacked by oxidising agents such as nitric acid or chromic acid. On distilling in a current of dry hydrogen a product was obtained which melted at 112° - 113° and had a boiling-point of 290° C., being similar in these respects to fluorene,



Further, it gave no depression of the freezing-point when mixed with fluorene. To determine whether the extracted substance were hexahydrofluorene or tetrahydrodiphenylmethane (both of which give hydrogen and fluorene on heating), the action of bromine was tried when mono- and di-bromofluorene were obtained. Oxidation with permanganate gave adipic, oxalic, and acetic acids. This necessitates that four of the additional hydrogen atoms be in one ring and two in the other. The formula is therefore either—



After further examination formula II. was determined upon.

These researches are interesting as definitely proving that hydrocarbons pre-exist as such in coal, and are not formed only on destructive distillation, a question on which there has been much debate.

Phenol was used as a solvent by Guignet,³⁵ and by its means he extracted 4 per cent. from a coal. On treating the extract with nitric acid he obtained oxalic acid and trinitroresorcin. He considered the extract to consist of resinous constituents of the coal.

Pyridine.—Baker³⁶ in 1900 made the interesting discovery that pyridine can be used as a solvent for coal, extracting very considerable quantities, the solution being brownish-red with greenish fluorescence. The soluble matter can be precipitated with hydrochloric acid, and on ignition gives a highly intumescent coke, the extracted coal having practically no coking power. Bedson,³⁷ continuing these researches, obtained extracts up to 35 per cent. of the coal (calculated as dry and ash-free), and found that, in general, coals with the largest proportion of soluble matter gave the best cokes. He showed that while the bright coal from a Durham seam contained 19.38 per cent. extractable matter, the “dant” or dull coal, which had properties similar to anthracite, contained less than one per cent. extractable matter. Anderson³⁸ gives analyses of extracts obtained from different coals as follows:—

	Extract from		
	Barakar (Bengal) Coal.	Yubari (Japan) Coal.	Bannockburn Main Coal.
H	5.82	6.12	6.05
C	82.91	81.51	83.39
O	8.73	10.00	7.30
N	2.24	2.17	2.86
S	0.30	0.20	0.40

The carbon percentage is usually less, and sometimes markedly so, than in the original coal, so that the bodies richer in carbon seem to form the bulk of the insoluble matter. In coals of inferior coking quality extraction with pyridine entirely removed the coking property, but in strong-coking coals a certain fusible constituent was left undissolved. The Scottish oil-shales also contain a substance or substances extractable by pyridine. The writer³⁹ obtained the following figures:—

	Extract from	
	Torbanite.	Broxburn Shale.
H	9.02	11.75
C	82.57	82.49
O	7.03	...
N	1.00	...
S	0.38	...

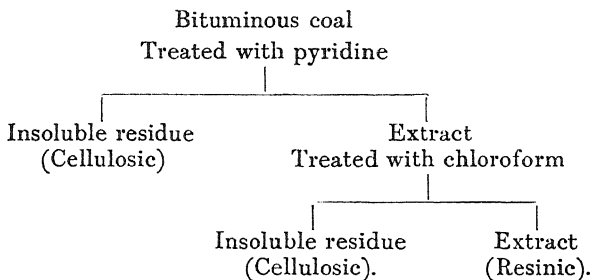
The carbon-hydrogen ratios here are lower than those of the extracts obtained from coals by Anderson. This fact suggests that at least some of the organic matter in oil-shales is similar to that in coals, but

differs in not having advanced so far in the process of loss of hydrogen and enrichment in carbon.

Wheeler and Burgess⁴⁰ made a large number of pyridine extractions, experimenting on fifty-two coals. The percentages extracted (calculated on ash-free dry coal) varied from 3.7 per cent. to 38.8 per cent. A remarkable relation was found between the amount of soluble material in the coal and the temperature at which the respective coal-dusts ignited, the temperature of ignition being found to increase with decreasing percentages of extractable material. The authors hesitate to affirm that this material can be absolutely identified with the readily decomposed paraffin-yielding constituents of coal, but as the extract on distillation yielded a mixture of hydrocarbons and hydrogen, whereas the residue insoluble in pyridine gave mainly hydrogen, carbon monoxide, and carbon dioxide, they consider their results in the main favourable to such a view. Clark and Wheeler⁴¹ found subsequently that pyridine only makes a partial separation between the two constituents of coal termed by them "humus" and "resinous" bodies respectively. The extract contains practically all the "resinous" material, but, in addition, a considerable portion of substances similar in properties to the insoluble (in other solvents) "humus" substances. If the extract is treated with chloroform or benzene about one-third of it dissolves, of which 80 per cent. is volatile on ignition. The residue behaves similarly to the original insoluble-in-pyridine residue. For example, 100 grams of coal were treated in a Soxhlet apparatus with pyridine

for several weeks. 20 grams were extracted. The original coal contained 34.7 per cent. volatile matter, the extract 53.3 per cent., and the residue 32.2 per cent. 10 grams of the extract on treatment with chloroform in the Soxhlet apparatus for fourteen days gave a deep orange-red and strongly fluorescent extract containing 4 grams extracted matter. This, on ignition, gave 85.6 per cent., and the residue only 31.4 per cent. volatile matter. The different extracts and residues were left in contact with photographic plates for some time and the plates then developed. The portion insoluble in pyridine gave only a faintly visible image, the portion soluble in pyridine gave a strong image of the same shape and size as the powder, while the portion soluble both in pyridine and chloroform gave a strong image with an extensive halo, and the portion soluble in pyridine but insoluble in chloroform no image at all. Russell⁴² showed that resin had an action on a photographic plate, the action being apparently due to some gas or vapour, for interposition of a thin sheet of mica, glass, or aluminium prevented direct action on the plate, although action took place round the edges of the interposed material as if a gas had crept round. Further, if a current of air after being passed through powdered resin were caused to impinge on the plate action took place. He also found that if a surface of ordinary coal were polished and placed on a photographic plate for sixteen hours at a temperature of 40°-50° C., on subsequent development the structure of the coal was shown up as streaks and patches of different intensity. Clark and Wheeler

therefore conclude that the portion of the coal soluble in both pyridine and chloroform is in all probability of a resinous nature. The nature of the separation is therefore as follows:—



Conclusions.—Organic solvents have, in general, little extractive power on coal. Several hydrocarbons have, however, been obtained with different solvents, proving that some coals, at least, contain these in their natural state. Pyridine has the greatest solvent action, extracting a mixture consisting of all the “resinous” constituents along with certain “cellulosic” materials.

IV.

THE OXIDATION OF COAL.

Atmospheric Oxidation. — It has for long been recognised that coal, on standing for some time exposed to atmospheric influences, undergoes change in several respects. Its calorific power becomes in general reduced, and frequently also its gas-producing and coking qualities. This change may represent a considerable loss in value to the coal-owner. The spontaneous heating and occasional ignition of coal stored in large quantities or confined in a ship's hold during transport is a source of danger towards the removing of which much investigation has been directed.

It was early found that "weathered" coal (*i.e.*, coal which had for some time been exposed to atmospheric conditions) was richer in oxygen and poorer in carbon and hydrogen than the original coal as removed from the mine. Richters⁴³ found that dry, powdered coal on being heated to 180°-200° increased in weight for a certain time (about twenty hours), after which there was a small loss in heat value, the weight and composition of the coal finally becoming constant. With the increase in weight there was also an increase in density and in non-

volatile material. Coking coals lost their coking property. By passing dry, CO_2 -free air over a weighed quantity of coal in a U-tube heated to 190° for ten hours and passing the exit gases through calcium chloride and soda-lime absorption tubes, it was found that all the carbon and hydrogen lost by the coal had been converted into carbon dioxide and water. That oxygen also combined with the coal substance itself and remained there in a fixed condition was shown by the change in the percentage of non-volatile matter, the strongly acid nature of the gas evolved on ignition, and the increase in density of the coal. It was found that the quantity of combined oxygen was in each case very much more than that evolved as carbon dioxide and water. Richters also showed that at ordinary temperatures oxygen was absorbed by coal both from dry and from moist air. Although these researches prove that the absorption of oxygen is not merely a physical process, yet the extent of surface per unit weight of coal has considerable influence, as the adsorption of oxygen aids considerably in its ultimate combination with the coal. Richters found that, although the rate of oxygen absorption is not proportional to the surface area of the coal, yet in every case it increased as the coal was more finely divided. The absorption of oxygen by fresh coal decreases with the passage of time. In order to determine whether this is due to the presence of the carbon dioxide formed in the oxidation, and, if so, to what extent, Richters made experiments which showed that, although increase in carbon dioxide did, in fact, temporarily reduce the

absorption of oxygen, it was not the final cause of the cessation of the reaction. If fresh coal is saturated with carbon dioxide and then placed in a tube filled with air and sealed with mercury, the carbon dioxide is gradually evolved, absorption of oxygen taking place as this proceeds. The progress of this interchange can be followed by absorbing the evolved carbon dioxide with caustic alkali introduced into the tube. The carbon-dioxide-saturated coal can also recover its property of absorbing oxygen by leaving it for some time in a vacuum, or by boiling it in water. But, if similar experiments are carried out with coal which has been weathered for a long time, although placing in a vacuum or boiling in water raises its absorbing power in a small degree, in no case is it made equal to that of fresh coal which has been saturated with carbon dioxide. It is thus shown that the absorption of oxygen is due to some constituent of the coal which is easily oxidised, and that when this has been completely oxidised further absorption of oxygen automatically ceases.

Boudouard ⁴⁴ found that if two samples of the same coal were exposed to air, that which had the longer exposure gave the poorest coke. It is therefore evident that it is the constituents responsible for the coking properties of a coal that are the most readily oxidised. Boudouard considers these to be hydrates of carbon which are oxidised on contact with air into humic acids. These acids are analogous to those obtained by acting on sugars with warm acids. ⁴⁵

The changes taking place in weathering are

summed up as follows by Muck:⁴⁶—(1) Weathering is the result of an absorption of oxygen, part of which oxidises the carbon and hydrogen of the coal to carbon dioxide and water, and part of which becomes chemically united with the coal substance. (2) The weathering process begins with an absorption of oxygen. Should the coal become heated on account of this or some other cause, the chemical reaction of the oxygen on the combustible part of the coal becomes more or less energetic in proportion to the extent of the temperature rise; otherwise the oxidation process is so slow that in the greater number of cases any change in the technical or analytical properties of the coal can scarcely be detected with surety after the lapse of a year. (3) Moisture as such has no direct influence on the rate of weathering. It should be noted, however, that many coals, especially those rich in easily decomposable iron pyrites, or which soon disintegrate in contact with water, become heated considerably more rapidly in damp than in dry conditions. (4) As long as the temperature does not exceed 170° - 190° , there is no marked loss of weight by weathering. The retention of oxygen by the coal frequently results in a small increase in weight. (5) To explain the reduction in calorific value, in coking value, in caking quality, and in gas-producing properties which coals suffer on weathering, it is not necessary in most cases to assume "a new grouping of atoms." Rather can these changes be explained by the loss in carbon and hydrogen and the gain in oxygen which result from the weathering.

Researches on the atmospheric oxidation of coal involve a considerable period of time for their completion. By means of chemical oxidising reagents results can be obtained more rapidly.

Potassium chlorate and hydrochloric acid attack coal with the production of chlorinated oxidation products. Smythe⁴⁷ found that if coal were boiled with dilute hydrochloric acid with addition of potassium chlorate from time to time, the coal gained in weight. 30 to 35 per cent. was then soluble in alcohol or acetone. On distilling off the solvent a reddish-brown resinous mass was left. This was extracted first with benzene and then with alcohol. The portion soluble in benzene gave on analysis the formula $C_{30}H_{22}Cl_8O_{10}$, and the portion insoluble in benzene but soluble in alcohol the formula $C_{24}H_{18}Cl_4O_9$. In the insoluble residue were found two substances giving the formulæ $C_{22}H_{14}Cl_3O_5$ and $C_{25}H_{20}Cl_3O_8$. The acid filtrate from the coal was extracted with acetone, and a yellow liquid obtained having the formula $C_{35}H_{36}Cl_4O_{20}$. These substances appeared to be acidic in nature, forming dark brown solutions with caustic alkalis and with ammonia, from which dark-coloured, gelatinous salts could be precipitated by means of barium chloride, lead nitrate, silver nitrate, etc.

Nitric Acid.—The action of nitric acid on coal has been studied by several experimenters. Guignet⁴⁸ treated the matter extracted by phenol from a coal with concentrated nitric acid. This matter amounted to 4 per cent. of the coal. The products obtained were oxalic acid and trinitroresorcin. He also

found⁴⁹ that brown coal was completely soluble in nitric acid, and that bituminous coal went partly into solution giving oxalic acid and trinitroresorcin and leaving a residue consisting of a mixture of nitrated products (which behaved like nitrated cellulose on heating), and substances of a humic nature.

Friswell⁵⁰ states that he covered bituminous coal in a fine powder with rather more than double its weight of 49 per cent. nitric acid, when the mass rapidly became warm, and dense red fumes were evolved. After the first reaction ceased, he heated the mixture gradually, raising it to boiling-point after six hours. It was then diluted and filtered. The residue was apparently unchanged coal, but, on boiling it with dilute sodium carbonate solution, nearly the whole dissolved, carbon dioxide being briskly evolved. The resulting solution was of a deep brown colour and filtered with difficulty. The residue was found to consist of coarse particles of coal, mixed with sand, etc. In other experiments with smaller quantities of more finely divided coal the author was able to bring the whole of the coal into solution. If the filtrate was treated with hydrochloric acid, a bulky deep brown to black flocculent precipitate formed. This was insoluble in water containing even small quantities of salts or acids, but was fairly soluble in boiling distilled water, separating out again as brown flocks on cooling. On drying at 100°, the precipitate formed a brilliant, black, friable mass with a conchoidal fracture. On heating, this puffed up and left a residue of carbon (thus resembling nitro-compounds), but efforts at

reduction with zinc and caustic soda and with sodium amalgam were unsuccessful. On dry distillation with zinc-dust, hydrogen and cyanogen were evolved, and there was a small aqueous distillate containing ammonia, pyridine, and much hydrocyanic acid. The author concludes that although the substance bears a certain resemblance to humic acids, it differs from these in being non-hygroscopic, in not becoming insoluble on drying, in not giving acetic acid on dry distillation, and in not yielding ammonia when boiled with alkalis, and is more probably a new nitro-compound.

Carrick Anderson⁵¹ found that if excess of acid were used, the same substance was always obtained, whether the excess were great or small. The coals examined by him dissolved almost completely when evaporated with nitric acid, and then treated with ammonia. The residue consisted of mineral matter surrounding particles of the "coal acid." He gives the following analyses of the "coal acids" (ash-free) obtained by him from Scottish coals:—

	Acid from						
	Ell.	Splint.	Gas.	Virgin.	Lower Drungray.	Bannock- burn.	Kilsyth coking.
H	3·17	3·24	3·20	2·78	2·99	3·35	3·18
C	58·76	63·17	61·93	59·78	63·93	63·05	61·75
O	32·53	28·42	29·43	33·11	28·25	28·72	31·01
N	4·82	4·85	4·75	4·05	4·31	4·45	3·32
S	0·72	0·32	0·69	0·28	0·52	0·43	0·74

The presence of sulphur in the coal acids he takes as proof of the existence of organic sulphur in

the coal. He also found that, on heating coal to 300°-310°, although there was a considerable loss in weight of the coal, the acid obtained after heating was practically identical in analysis with that of the original coal, and concludes that the nitrogenous constituent in coal therefore remains intact at that temperature. This conclusion would not hold if the "coal acid" should be a nitrated compound as Friswell suggests.

Donath⁵² found that, on treating brown coal with dilute nitric acid, action took place at about 70° with evolution of much gas and further heating of the solution. The gases evolved were carbon dioxide, hydrocyanic acid, oxides of nitrogen, and nitrogen itself (40 per cent. of the whole gas). There were found in solution formic, acetic, and higher fatty acids, oxalic acid, and ammonium salts. The solution was of the colour of a saturated solution of potassium bichromate. Anthracite, similarly treated, gave no reaction on heating on a water-bath. On the sand-bath there was a weak evolution of carbon dioxide and nitrous fumes. The author concludes that lignite and anthracite are of entirely different origins.

The writer⁵³ tried the action of nitric acid on the following materials:—(1) Torbanite; (2) Broxburn oil-shale; (3) Newbattle cannel coal; (4) Glenfalloch peat; (5) Lycopodium spore dust; and (6) an organic sludge consisting of decomposed leaf and root remains, microscopic algæ, diatoms, and bacteria. It was found impossible to sufficiently moderate the action of the acid on the sludge, the whole of the oxidisable

matter being converted into carbon dioxide, oxalic acid, etc. In the other cases, the finely divided material was evaporated to dryness with excess of concentrated nitric acid and the solid residue treated with ammonia solution, in which most of it dissolved. The insoluble part was filtered off, and the solution treated with dilute hydrochloric acid. A precipitate was obtained in each case, that from lycopodium being light brown, and those from the peat, cannel coal, oil-shale, and torbanite dark brown in colour. The precipitates were filtered off, washed with water, and dried in a vacuum, when all became hard and brittle except that from lycopodium, which was of a gummy consistency. They all contained traces of sulphur and a small amount of ash. On analysis they gave (neglecting sulphur and calculating as ash-free)—

	Acid from				
	Torbanite.	Broxburn Shale.	Cannel Coal.	Peat.	Lycopodium.
C	61.26	59.62	58.61	52.93	60.15
H	7.42	6.72	5.44	5.47	9.39
N	4.37	4.29	3.92	4.59	3.80
O	26.95	29.37	37.03	37.01	26.66

It was found that these acids formed insoluble salts with some metallic radicals such as silver, lead, copper, iron, cobalt, and barium. Analysis of silver and ammonium salts pointed to the following empirical formulæ for the acids:—

Acid from Torbanite . .	$C_{16}H_{24}NO_5$
„ Broxburn shale . .	$C_{16}H_{22}NO_6$
„ Cannel coal . .	$C_{16}H_{19}NO_8$
„ Peat . .	$C_{13}H_{17}NO_7$
„ Lycopodium . .	$C_{19}H_{35}NO_6$

The substances appeared to be all of a similar nature, and to form a series from lycopodium acid, with the highest hydrogen percentage, through torbanite, Broxburn shale, and peat acids to cannel-coal acid, with the lowest. Carrick Anderson's coal-acid analyses would give formulæ from $C_{14}H_9NO_6$ (Ell) to $C_{21}H_{13}NO_8$ (Kilsyth coking), so that the various bituminous coals might be considered as some of the next members of the series. These facts seem to point to a close relationship of character in the constituents of the different coals and allied materials.

Conclusions.—All these researches point to the following conclusions:—

- (1) There is a constituent in cannel coals and bituminous coals which is easily oxidisable by air. This constituent is probably of a resinous nature, oxidation of which results in humic acids.
- (2) Most if not all the constituents of coal are soluble in strong oxidising agents such as potassium chlorate and hydrochloric acid, nitric acid, etc., there being formed either chlorinated or nitrated products of complex constitution and which are more or less typical of the coal used.

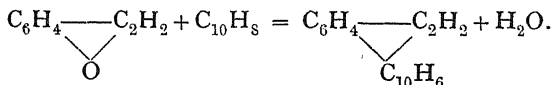
V.

THE DESTRUCTIVE DISTILLATION OF COAL.

THE destructive distillation of coal at ordinary pressures is a process of great technical importance, and the products obtained by this means are many and varied. Their nature casts a certain amount of light on the composition of coal, but the process of distillation takes place at a somewhat high temperature, and the decomposition is such that it is probably well within the mark to say that of the several hundred recognised products of distillation not more than a few of the gases evolved and of the simpler hydrocarbons exist as such in the coal before distillation. It has, however, been found possible, by means of carrying out the distillation in a vacuum or under reduced pressure, to isolate several constituents of coal in an unaltered form, and in other cases to obtain products much nearer to the original coal constituents than those obtained by distillation at ordinary pressures, and on which it is therefore possible to build up reasonable hypotheses as to the chemical nature of the coal substance or substances.

Vacuum Tar.—Several experimenters have followed the procedure of first obtaining a “vacuum-tar” by distilling the coal under reduced pressure, and then

endeavouring by various means, such as the action of solvents or fractional distillation, to isolate constituents of this tar. The process presents many difficulties in practice. For instance, Pictet and Bouvier⁵⁴ found that on fractionally distilling vacuum tar there was in general a polymerisation during the process, especially in the higher fractions, whereby with each distillation the higher-boiling portions were increased at the expense of the lower-boiling ones. Thus simple members of a homogeneous series may be converted into higher and more complex ones. It is therefore apparent that, although the distillation of coal even at reduced pressures must be considered essentially as a destructive process producing compounds of a relatively simple nature, yet, at the same time, polymerisation may be taking place, a tar of very complex nature being thereby produced. This, of course, adds to the difficulties of analysis, and at the same time may lead to the formation of false conclusions regarding the original constituents of the coal. Berthelot showed in 1870 that benzene could be synthesised by passing acetylene through a red-hot tube. Krämer and Spilker⁵⁵ have shown that an interesting condensation takes place when cumarone and naphthalene are distilled together, crysene being formed thus:—



Crysene is a constituent of coal-tar. These two examples may serve to show the complexity of the problems involved in the examination of vacuum tar.

We shall now proceed to describe in detail some of the substances produced on distillation of coal in a vacuum or under reduced pressure and point out their bearing on the composition of coal.

Paraffins.—Burgess and Wheeler⁵⁶ found that, on commencing a distillation in vacuum, the first products evolved were paraffins which were probably present in the coal as occluded or “condensed” gases not extractable at atmospheric pressure. This evolution occurred at temperatures of 150°-200°. The paraffins present were mainly the members of the series up to pentane. Above 300° the percentage of methane in the gases increases, while that of the higher paraffins falls off. The authors think it conceivable that the paraffins evolved below 300° are present as such in the coal, being occluded in a similar fashion to methane at lower temperatures, but, as olefines are also evolved to a certain extent, consider that it is also possible that both paraffins and olefines arise from the decomposition of a solid paraffin or similar long-chain compound.

Jones and Wheeler,⁵⁷ by distillation of a bituminous coal under 5-40 mms. pressure, obtained a solid paraffin in small quantity. It melted at 52·5°-54° and had a molecular weight of 373·7, which lies between those of $C_{26}H_{54}$ and $C_{27}H_{56}$. Pictet and Bouvier⁵⁸ obtained no solid paraffins from distillations of French coal at 15-17 mms. pressure. This may be due to the difference in method of distillation to that used by Jones and Wheeler. That of Pictet and Bouvier lasted for five hours, whereas Jones and Wheeler's distillation was continued for

weeks. On the other hand, it is probably due to differences in the coals employed. Jones and Wheeler obtained free solid paraffins from coal by treating the extracts obtained by pyridine and chloroform with pentane, which dissolved out a paraffin wax of melting-point 55° - 59° . This amounted to 0.10 per cent. of the total weight of the coal. They point out, however, that the presence of this paraffin may have been caused by previous heating of the coal resulting from faulting due to earth movements. The existence of free paraffins in coal is therefore, although exceedingly probable, not yet definitely proved.

Olefines.—These are present in the gases formed when coal is distilled at atmospheric pressure. They occur also in considerable quantity on vacuum distillation. Thus Jones and Wheeler,⁵⁹ on distilling coal in a vacuum at 350° , obtained 1.25 per cent. of tar, which on redistillation gave 44 per cent. olefines in the fraction 170° - 250° and 56 per cent. olefines in the fraction 250° - 300° .

Benzene and Homologues.—Although benzene is an important constituent of the coal distillate at ordinary pressures, Jones and Wheeler⁶⁰ found it to be absent from the tar obtained in their distillation of bituminous coal at temperatures up to 430° .

Phenols.—Jones and Wheeler⁶¹ found 17 per cent. phenols in vacuum tar obtained from coal at 350° and 12 to 15 per cent. phenols (chiefly cresols and xylenols) from similar tars obtained at 430° .

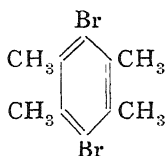
Homologues of naphthalene were present to the extent of about 7 per cent. of the tar. Naphthalene itself did not appear to be present. The presence of

naphthalene or its homologues can be demonstrated by aspirating the vapour from the oils at 100° through a solution of picric acid, when yellow crystals of addition compounds are formed. Pictet and Bouvier,⁶² however, assert that naphthalene, anthracene, and other solid aromatic hydrocarbons are almost entirely absent from vacuum tars, none being obtained by them as crystals on cooling their tar fractions. On distilling the tar, however, in a tube heated to redness and at atmospheric pressure, benzene, naphthalene, and anthracene were all found in the distillate. They therefore conclude that their vacuum tar is an intermediate product in the distillation of ordinary tar, and that it is formed in the retorts at temperatures below 450°, higher temperatures producing a pyrogenic decomposition.

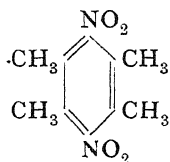
Hexahydromesitylene and Hexahydrodurol.—Pictet and Bouvier⁶³ claim to have separated and identified these compounds in the course of their examination of vacuum tar by the following procedure. Each fraction obtained by distillation of the tar was heated over sodium under a reflux condensor in order to extract all oxygen-containing compounds. White or bright yellow compounds were formed. They were filtered off, washed with ether, and after being treated with a little alcohol to remove excess of sodium, were hydrolytically decomposed with cold water. Oils were obtained which were purified by distillation at ordinary pressure. They were pleasant-smelling (like menthol), difficultly soluble in water, and insoluble in alcohol. They evolved hydrochloric acid on treatment with acetyl- or benzoyl-chloride,

liquid esters being formed which did not further react with sodium. After thus removing these alcohols, the mixture of hydrocarbons left was found instantly to decolorise potassium permanganate or bromine in carbon disulphide solution. Unsaturated hydrocarbons were thus indicated, and these were removed by means of fuming sulphuric acid. The remaining hydrocarbons were again heated with sodium to remove oxidised products, and then rectified several times. The saturated hydrocarbons thus obtained constituted 20 to 40 per cent. of the original oils. As the authors were looking for decahydronaphthalene, which they supposed to be the mother substance of the naphthalene of tars, they further examined the portions of distillate boiling at 172°-174° and at 189°-191°, the boiling-point of decahydronaphthalene being given as 173°-180° by Wreden and as 189°-191° by Ipatiev. Both these fractions, on ultimate analysis, gave empirical formulæ corresponding to C_nH_{2n} . Neither could therefore be decahydronaphthalene ($C_{10}H_{18}$). Both were saturated hydrocarbons, and therefore belonged to the cycloparaffins. Molecular weight determinations made cryoscopically in benzene were found to give the formulæ $C_{10}H_{20}$ and $C_{11}H_{22}$ respectively. Both fractions were colourless and non-fluorescent, practically insoluble in water but miscible in all proportions with the common organic solvents. Similar compounds had been found by Mabery⁶⁴ in Canadian petroleums. The structure of the compounds was investigated. Oxidising agents split the ring with formation of fatty acids. Bromine vapour was

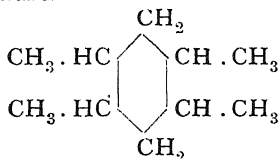
allowed to react in the cold on the first of these compounds. Hydrobromic acid was evolved, and beautiful, long, colourless needles formed. These had a melting-point of 202° , which agrees with that found by Friedel and Crafts for dibromdurol—



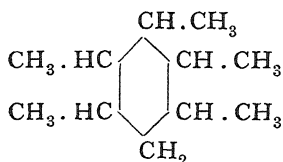
Further, the vapour of the $C_{10}H_{20}$ compound was led over iron oxide heated to dull redness. A fluid distillate was obtained. This was nitrated with nitric acid of 1.52 density, when a yellow nitro compound melting at 202° was obtained, dinitrodurol—



which, according to Nef, melts at 205° . The formula for hexahydrodurol



is therefore given by the authors to this substance, and that of the hexahydrate of pentamethylbenzene



to the compound $\text{C}_{11}\text{H}_{22}$. Further examination of the distillates⁶⁵ gave the chief fractions as those boiling at $135^\circ\text{--}137^\circ$, $160^\circ\text{--}161^\circ$, $172^\circ\text{--}174^\circ$, $189^\circ\text{--}191^\circ$, $211^\circ\text{--}213^\circ$, and $227^\circ\text{--}229^\circ$, having the molecular weights C_9H_{18} , $\text{C}_{10}\text{H}_{20}$, $\text{C}_{10}\text{H}_{20}$, $\text{C}_{11}\text{H}_{22}$, $\text{C}_{12}\text{H}_{24}$, and $\text{C}_{13}\text{H}_{26}$ respectively. The residue partially crystallised on standing. The crystals were separated, recrystallised from acetone, and the molecular weight of $\text{C}_{30}\text{H}_{60}$ found. This substance was also obtained by Pictet and Ramseyer⁶⁶ by extraction of coal with benzol, and therefore probably pre-exists in the coal. It is also obtained from Galician petroleum and from beeswax (therefore named Melen). The different cycloparaffins obtained can be tabulated as follows:—

	B.P.	Density.	Also existing in
C_9H_{18} Hexahydromesitylene	$135^\circ\text{--}7^\circ$	·7590	{ Californian petroleum.
$\text{C}_{10}\text{H}_{20}$.	$160^\circ\text{--}1^\circ$	·7680	
$\text{C}_{10}\text{H}_{20}$ Hexahydrodurol .	$172^\circ\text{--}4^\circ$	·7765	{ Canadian petroleum.
$\text{C}_{11}\text{H}_{22}$.	$189^\circ\text{--}91^\circ$	·7838	
$\text{C}_{12}\text{H}_{24}$.	$211^\circ\text{--}13^\circ$	·7862	" "
$\text{C}_{13}\text{H}_{26}$.	$227^\circ\text{--}9^\circ$	·7953	
$\text{C}_{30}\text{H}_{60}$ Melen . . .	$218^\circ(\cdot 5\text{mm.})$	·9128	{ Galician petroleum.

Pyridine.—Jones and Wheeler⁶⁷ found pyridine in one of the fractions obtained by distillation of

vacuum tar, but it was present only in traces. It is not mentioned by other writers as being present. It is therefore very likely that its formation by destructive distillation at ordinary pressures, and presence in quantity in ordinary coal-tars are due to the further decomposition of some intermediate product, which is stable only at relatively low temperatures.

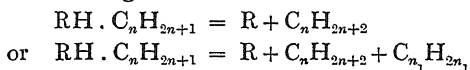
Unsaturated Hydrocarbons.—From the vacuum tar obtained below 430° , the oils boiling below 300° and constituting about one-half of the whole, were found by Jones and Wheeler⁶⁸ to consist of from 40 per cent. to 45 per cent. of unsaturated ethylenic hydrocarbons.

Distillation of Different Constituents of Coal.—As already shown, coal may be separated into parts of different properties by means of extraction with various solvents, in particular by means of pyridine. Some interesting points have been demonstrated by the vacuum distillation of these portions. Jones and Wheeler⁶⁹ carried through a research as follows:—About a kilogram of coal was extracted with pyridine. The residue was dried over sulphuric acid in vacuum, and then distilled in a vacuum. The distillate gave only a small percentage of liquid products, and these were mainly phenols. The pyridine solution was concentrated in a vacuum, and when it became viscous was poured into water. The chocolate-brown precipitate which formed was extracted with chloroform. The residue, after drying in a vacuum, was distilled similarly to the first residue. Here again the distillate consisted only of a small percentage of liquid products of which 40

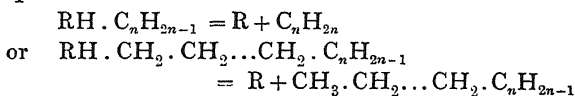
per cent. were phenols and the rest of a resinous nature possibly arising from some incompletely extracted coal mixed with the material in the flask. The chloroform extract was evaporated to dryness in vacuum at 100°. The extracted material softened at 90° and portions melted at 102°. On distillation in vacuum gases were evolved at 107°. The oil collected up to 180° gave on analysis C, 86.50; H, 9.88; C+H, 96.38. The oxygen present was not there as phenolic oxygen. At 250° considerable paraffin wax distilled over mixed with some resinous material whose proportion increased with increasing temperature. The distillation was continued to 400°. A hard, compact pitch was left in the flask, whereas in the two previous distillations there was no tendency for the residue to cake. This shows the coking properties of coal to be due to the resinous constituents. It is also shown that the resinous constituents are responsible for the main bulk of the liquid distillates, the humic substances, however, giving a small portion of distinctive character, *i.e.* containing phenols.

Theory of "Bound" Molecules.—To account for these various products of coal distillation under reduced pressure, and for the fact that few of them can be extracted from coal by common organic solvents, Jones and Wheeler have formulated an elaborate hypothesis, which they designate as the theory of "bound" molecules. They point out, first of all, that the liquid and gaseous paraffins formed on distillation cannot be formed by the decomposition of solid paraffins pre-existing in the coal, as these

are very insufficient in quantity. They consider it improbable that they are formed by rapid pyrogenic synthesis during the distillation. This view is supported by the researches of Pictet and Bouvier. They therefore suppose that the paraffins are originally present in some such manner that while in a sense they are structurally complete, yet some slight change in their state is necessary before they are liberated, and that this change can be produced by moderate heat. Thus they may be "bound" as alkyl or paraffinoid groups chemically attached to another non-alkyl group R. H, the compounds having therefore the general formula $RH \cdot C_nH_{2n+1}$ where n may have any value up to 32 or even higher. On distillation, "free" paraffins may be readily formed according to the formula:—

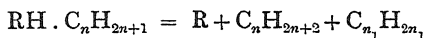


A similar explanation can be made of the presence of naphthalenes. Thus:—



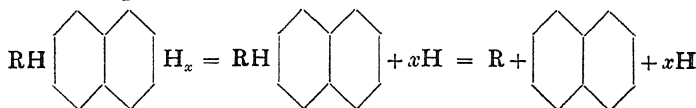
The original compounds here would be of the saturated ring variety, and, as it has been shown by Ipatiev⁷⁰ and others, that by means of combined heat and pressure ethylenes can be caused to condense or isomerise into naphthenes, it is quite possible that such conditions have produced saturated ringed carbon compounds during the formation of coal. The presence of ethylenes in coal distillates can be accounted for either by the breaking down of

highly polymerised ethylenic compounds or by the equation

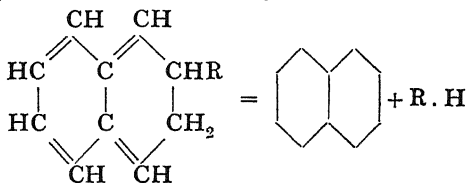


already referred to.

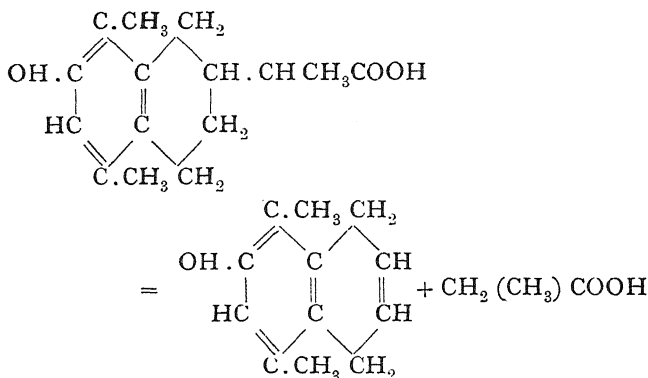
The presence of naphthalene compounds and absence of benzene in the distillates obtained by Jones and Wheeler is explained by them thus:—Although the "bound" hypothesis may be equally applied to both compounds, yet, while dihydronaphthalene decomposes at 400° giving naphthalene and hydrogen, hexahydrobenzene remains undecomposed at 450°, which was the maximum temperature used in the distillations. If, therefore, both hydrogenated naphthalene and hydrogenated benzene groups were present in coal in the "bound" condition, only the former would eliminate hydrogen and thus become free according to the equation—



It was found on further experiment⁷¹ that naphthalenes could be obtained by distillation in vacuum at temperatures as low as 350°. This would not be possible according to the above equation, and the authors therefore modify it so that elimination of hydrogen does not necessarily occur. Thus:—



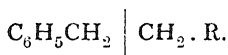
The possibility of such a reaction they deduce from the mechanism of the decomposition of santonic acid ($C_{15}H_{20}O_3$), which, according to Cannizzaro,⁷² breaks up between 300° and 350° thus:—



The case of phenols is more difficult of explanation, as "bound" compounds containing an OH group should be soluble in caustic potash. Russig⁷³ suggests that phenols might arise from the decomposition of polymerised coumarones, and Kraemer and Spilker⁷⁴ showed that *p*-coumarone (C_8H_6O)₄ at 300° gives 17 per cent. phenol and 52 per cent. coumarone. Jones and Wheeler, however, observed no coumarones in any of their distillates.

Brooks and Humphrey⁷⁵ consider the formation of naphthalene at temperatures as low as 350° better accounted for by assuming the decomposition of a complex molecule containing the naphthalene radical in the same way as they have shown phenyl-paraffin to be broken down into benzene, toluene, and unsaturated hydrocarbons. They prepared synthetic

phenyl-paraffin by chlorinating a paraffin of mean molecular formula $C_{24}H_{50}$ to $C_{24}H_{49}Cl$ and then treating this with benzene and anhydrous aluminium chloride. By heating to 250° the excess benzene was removed. On further heating the dried material with aluminium chloride to between 200° and 240° , both benzene and toluene were found in the distillate. The presence of the toluene could only be accounted for by the splitting of the phenyl-paraffin between two CH_2 groups thus:—



The residue was also found to consist of a mixture of naphthenes. The formation of naphthalene in coal distillation can therefore be represented by the equation—



Distillation of Coal at Ordinary Pressures.—The study of the products of distillation at ordinary pressures and different temperatures gives some important information as to the structure of coal. The observations made by Vignon,⁷⁶ who experimented on Montrambert and other coals, can be summarised as follows:—

- (1) Unsaturated hydrocarbons are evolved at temperatures chiefly below 600° . They disappear entirely at high temperatures.
- (2) Methane and other saturated hydrocarbons are abundant, comprising 60 to 84 per cent. of the gases up to about 800° , beyond

which temperature their proportion rapidly decreases.

- (3) Hydrogen is evolved in small quantity (2 to 25 per cent.) up to 600° , predominates from 800 - 1000° , and then diminishes up to 1200° .
- (4) Carbon monoxide varies from 3 to 11 per cent. in different samples up to 850° , thereafter rising in percentage until it may pass 30 per cent. above 1000° .

An exhaustive inquiry into the nature of the gases evolved on coal distillation was conducted by Wheeler and Burgess⁷⁷ in their investigations as to the causes of explosions in mines. By the destructive distillation of coal at atmospheric pressure and at various temperatures they demonstrated the following facts—

(1) With all coals, whether bituminous, semi-bituminous, or anthracitic, there is a well-defined decomposition point at a temperature lying between 700° and 800° which corresponds with a marked increase in the evolution of hydrogen. In bituminous coals this increase falls off above 900° , but in anthracites it is maintained up to 1100° . (2) Evolution of paraffin hydrocarbons ceases practically entirely at temperatures above 700° . (3) Ethane, propane, and butane, and probably higher members of the paraffin series form a large percentage of the gases evolved at temperatures below 450° . It is thus shown that there is a constituent in coal which decomposes rapidly at a temperature lying between 700° and 800° , giving hydrogen as its chief gaseous product. At

lower temperatures paraffin hydrocarbons are the chief products, and these may be due either to the decomposition of this same constituent in a different fashion, or to another constituent altogether which decomposes at low temperatures with formation of paraffins.

A second series of experiments in which the coal was rapidly raised to a definite temperature, and the gases evolved during successive stages of the distillation analysed, showed that in the first gases evolved, whether at temperatures above or below the critical temperature 700° - 800° , the paraffin hydrocarbons formed by far the largest proportions. The authors therefore conclude that coal contains two types of compounds of different degrees of ease of decomposition, the more unstable of the two yielding paraffins but no hydrogen, and the other, which decomposes with more difficulty, yielding hydrogen alone (or, possibly, hydrogen and oxides of carbon) as its chief decomposition product. This view was further confirmed by the fact that it was found possible by prolonged exhaustion at a low temperature to remove entirely the paraffin-yielding constituents, leaving only a compound which at higher temperatures evolved hydrogen. The authors consider that the chief differences in the properties of coals are due to the relative proportions in which these two constituents are blended. Anthracite, for example, might be looked upon as consisting almost entirely of the more stable, hydrogen-producing compound. It was also noticed in carrying out the above experiments that while the percentage of carbon monoxide

increased with increasing temperature of distillation, yet only the percentage present in the gases, and not its actual quantity, increased towards the end of a distillation at constant temperature. Thus the rate of formation of carbon monoxide is uniform during distillation at any one temperature being maintained while the evolution of other gases falls off. It is therefore probably due to the interaction of oxygenated compounds with the carbon of the coal, and not to the direct decomposition of these compounds—*e.g.*, it may arise through the elimination of water from hydroxy compounds, and the subsequent reaction of the steam so produced with the carbon of the coal.

Considering the undoubted vegetable origin of coal, the authors think themselves justified in assuming that one of the types of compound in coal, and that the most important, is a degradation product of cellulose. This they identify with the hydrogen-yielding component in coal, having regard to experiments made on the destructive distillation of cellulose and oxycellulose at high temperatures. They class the paraffin-yielding constituents as being derived from the resins and gums originally contained in the sap of the coal-forming plants.

Summary.—It is highly probable that free paraffins exist in coal. Cyclo-paraffins, such as hexahydromesitylene, hexahydrodurol, etc., are present either in a free state or in loose combination with other compounds. The “bound” hypothesis of Jones and Wheeler provides a likely explanation of the difficulty of extraction of coal constituents by

means of solvents, although these same constituents may be easily obtainable on vacuum distillation. Wheeler and Burgess, by examination of the gases evolved on coal distillation, have shown coal to consist of at least two types of compound of cellulosic and resinic nature respectively.

VI.

THE ANALYSIS OF COAL—SAMPLING.

COAL being of very great industrial and economic importance, it is necessary that the chemist in any industry which consumes a considerable quantity in its operations should be able to carry out trustworthy tests as to the quality of its supplies. It is also of importance for states which possess coal supplies within their borders, whether these are developed or undeveloped, to have concise information not only as to the extent of these deposits, but also as to their quality and their applicability to the various requirements of manufacture and trade. Accordingly much attention has been given to coal analysis both by private companies and by the State, and the methods of procedure have become fairly well standardised. This is indeed necessary, for the sampling and analysis of a coal is a matter full of pitfalls for the beginner, and there are many factors easy to overlook, which, if one omits to take into account, may cause serious error in the analytical results. It is proposed to give here an outline of the procedure commonly adopted, but it should be noted that different states or corporations in many cases employ somewhat different methods.

Especially is this the case in the proximate analysis of coal and in the determination of its calorific value.

Taking of the Coal Sample.—As the whole value of an analysis depends primarily on the securing of a correct sample, great care should always be taken to ensure that the sampling is carried out in such a way as to secure that the final few grams of coal used in analysis is a fair and just specimen of the several tons of material on which the test is being made. The picking up at random of a few pieces of coal from a large heap is in no case sufficient. In the first place, one is almost sure in following this procedure to select pieces of a definite size, such as are most easily powdered for analysis, thus neglecting both the larger lumps of coal and the fine dust which is usually to be found in quantity in coal deposits. Now both of these may differ greatly from the sample pieces taken. The large lumps have probably suffered less alteration by atmospheric action during their transport from the mine and their storage. For example, their moisture content is in all probability less than that of the smaller pieces. On the other hand, the coal-dust may have been altered to a great extent. It has probably diminished in calorific value due to atmospheric oxidation as pointed out in an earlier chapter, and it will have considerable hygroscopic moisture in excess of that attached to larger particles. If the coal is stacked in a large heap and has lain so for a considerable time, the exterior layers are sure to give different analytical results from the more central portions. The chemist must therefore either perform analyses on both these

parts, and so determine if the differences are sufficiently great to be of importance, or once for all secure one sample which he can confidently affirm to be representative of the whole. The size of the first sample to be taken will depend, of course, on the size of the coal consignment to be tested. If it consists of several truck- or cart-loads, several shovelfuls may be taken from each truck or cart during the process of unloading. It is always better to err on the side of having a large sample. The extra work involved in reducing it is well repaid by the increased certainty of its representative character. The sample is first broken up with a hammer into pieces about the size of a walnut. The whole is well mixed on a hard floor, and spread out evenly in the form of a square. The diagonals of the square are then drawn, thus dividing the coal into four parts, and of these two of the parts lying opposite each other are removed and the other two retained. This ensures that should the mixing not be quite perfect, and accordingly different parts of the square be of slightly different composition, there is yet an equal chance of any one fragment being taken or left, any discrepancy being thereby adjusted. The remaining coal is then further broken up, mixed, formed into a square, and sampled as before. This process is repeated as often as may be necessary until the remaining coal is of sufficient quantity (two pounds or more) to constitute a laboratory sample. Until required for analysis, this is placed in an air-tight vessel of such a size as to be practically filled with the coal.

It is customary to make analyses on "air-dried"

coal, that is on coal which has lain exposed to air at laboratory temperature and having a humidity of about 50 per cent., until constant weight is obtained. If desired, the gain or loss in weight of the whole sample may be measured, and this gives an indication of the moisture content of the coal below or above that of the laboratory air. This determination should be made just before finally grinding the sample for the proximate analysis. The sample is then ground in a ball-mill or in a large iron mortar to the state of a coarse grit, mixed, and quartered, then further ground, mixed, and quartered until about one hundred grams of fine powder (such as will pass through a sieve of four hundred meshes to the square centimetre) are left. This is stored in an air-tight bottle and portions used for each analysis, the bottle being well shaken each time before removing any coal.

The analysis of coal may be divided into three parts, namely—

- (1) Proximate analysis, including the determination of moisture, ash, volatile matter, and coke;
- (2) Ultimate analysis, including the determination of carbon, hydrogen, nitrogen, sulphur, phosphorus, and oxygen; and
- (3) The determination of the calorific value.

VII.

THE ANALYSIS OF COAL—PROXIMATE ANALYSIS.

Moisture.—The analyses for moisture and all the other components are usually made on the air-dried coal, and, if desired, the results can then be easily calculated for the original coal, if the extra moisture has been determined as described in the procedure of sampling. About one gram of the air-dried coal is weighed out in a watch-glass and then placed in an air-oven at a temperature of 105° C. for one hour. The oven must be kept at constant temperature by means of a thermo-regulator. The loss in weight represents the moisture present. In the case of coals which are easily oxidisable at low temperatures, *e.g.* lignites, it may be necessary to determine the moisture in a stream of carbon dioxide. This can be done by weighing out the coal in a porcelain boat, and placing this inside a glass tube which passes through the air-oven, and through which a slow stream of carbon dioxide can be led. The analysis should always be made in duplicate.

The valuation of the moisture in coal may vary very considerably according to the method employed. The International Commission on Analytical Methods⁷⁸ came to the following conclusions:—(1)

It is not possible by analysis to distinguish between added water, moisture (absorbed water and water condensed on the surface of the coal), and water of crystallisation contained in the coal. (2) It is probable that a distinction between moisture and combined water would signify but little, as determinations of moisture lost (a) at ordinary temperature and greatly reduced pressure in presence of a drying agent, and (b) at a temperature a little above the boiling-point of water and at atmospheric pressure, show no pronounced difference. (3) Since coals are often easily oxidisable, the most reliable results are obtained by carrying out the analysis in an oxygen-free atmosphere. (4) Since coal is very hygroscopic, it must, both during the period of attaining a state of air-dryness and afterwards, be carefully protected from changes of temperature or humidity. (5) The process of drying can be divided into two periods. During the first of these, drying proceeds very quickly, but finally it becomes very slow. It should therefore be continued until the difference between successive weighings becomes very small. (6) If the first drying takes place rapidly, the gain in weight due to absorption of oxygen can very easily exceed the loss in weight due to the more lengthy, subsequent water loss. (7) Heating the coal to less than 105° offers no advantages. They recommend that whenever possible, especially in the case of very moist coals, the water in the original sample should be estimated by one of the following methods, previous handling being reduced to a minimum. (A) A carefully weighed sample of 100-500 grams is spread out on a metal plate and

allowed to remain in the laboratory atmosphere for at least twenty-four hours. It is then weighed again and the difference in weight calculated as a percentage. The coal is then ground in a ball-mill and the moisture estimated as usual in air-dried samples. Thus the total percentage moisture and also the moisture left on air-drying are both determined. (B) Moisture is removed from the coal by heating in boiling xylol and the water which distils over with the xylol measured (see below). It is further recommended that the coal be dried in an air-oven with good circulation of air for at most one hour, at a temperature not below 104° or above 111° . The coal should be contained in a pair of close-fitting watch-glasses previously heated to the temperature of the oven and allowed to cool in a desiccator. During the heating of the coal, the upper glass is removed, being replaced on removing the sample from the oven. The whole is re-weighed after cooling in the desiccator. A suitable temperature in the air-bath is obtainable by the use of boiling toluene at atmospheric pressure, or of water at 906-1100 mm. pressure. An electrically heated thermostatic oven is also useful. Drying in vacuum over sulphuric acid or other drying agent has no advantage over the above procedure. It takes a much longer time, and, in letting air into the desiccator on each occasion, it must be carefully dried by bubbling through sulphuric acid. By removing the water from coal by heating in boiling xylol, it is possible to obtain a higher temperature (about 140°), and at the same time have an oxygen-free atmosphere.

From 50 to 100 grams should be weighed out into a 600 c.c. Erlenmeyer flask and 150-200 c.c. of xylol added, also a few pieces of pumice-stone to assist boiling. (The xylol should previously be saturated with water by shaking vigorously in a separating funnel with distilled water and leaving to stand overnight before separating.) The xylol is then distilled, the distillate being collected in a measuring cylinder until about 100 c.c. have passed over. The volume of water underlying the xylol is read to the nearest $\frac{1}{10}$ th of a c.c. and the percentage on the coal calculated. This method has the advantages that (1) a very large sample is required, thus ensuring an average moisture content, and (2) the water itself is measured directly. The results obtained are in general slightly higher than those found at lower temperatures.

Ash.—Two to five grams of the coal are used. This is heated in a platinum crucible, at first very gently so as to drive off the volatile matter at a low temperature and reduce the chance of the coal coking, and also of the loss of particles which might be carried off in the flame. The crucible should be fitted into a circular hole in an asbestos board. This prevents the gases from the burner surrounding the crucible and so cutting off the supply of air required for the combustion of the coal. After the volatile matter has been all evolved, the crucible is heated strongly to a bright red heat until all the carbon is burnt off. The whole combustion occupies in general two to three hours, but much longer time may be required if the coal is one which cokes easily, forming

large lumps which are difficult to heat to the centre. The heating may also be carried out in a muffle oven, especially if many analyses have to be performed. No dark, unburnt particles of coal should be visible in the ash, and it is advisable after weighing to ignite and weigh again to ensure that constant weight has been obtained. The presence of considerable sulphur in the coal may give rise to different results in the ash percentage, as the quantity of sulphur retained depends on the temperature, length of heating, and degree of access of air during ignition.

Coke and "Fixed Carbon."—One gram of finely powdered coal is heated in a platinum crucible at least $1\frac{1}{4}$ in. high and having a tightly-fitting cover. The flame used should be at least 7 in. high. The crucible should be supported on a triangle of thin platinum wire so that the space between the bottom of the crucible and the top of the bunsen burner is about $2\frac{1}{2}$ or 3 in. The heating should only be continued as long as any inflammable gas is evolved from the coal, and should in no case be of more than a few minutes' duration. The lower surface of the crucible lid will then be found to be coated with soot, but the exterior should be quite bright. If the crucible be too small or the platinum triangle too thick, high results will be obtained. The procedure varies somewhat in different countries and institutions, with corresponding variations in the results obtained. The coke percentage must therefore be considered not as an absolute but simply as a relative measure. The percentage of "fixed carbon" is obtained by

subtracting the ash percentage from the coke percentage.

Volatile Matter.—To obtain this the percentages of “fixed carbon,” ash, and moisture are subtracted from 100.

VIII.

THE ANALYSIS OF COAL—ULTIMATE ANALYSIS.

THE ultimate analysis of coal is not nearly so frequently carried out as the proximate analysis, the determination of sulphur being a possible exception. The proximate analysis gives the more useful data for industrial purposes and requires much less time and labour, but many facts of scientific interest are revealed by performing series of ultimate analyses. The methods employed are less strictly defined than those of proximate analysis, and several methods or modifications of procedure are applicable in determining the elements—carbon, hydrogen, nitrogen, sulphur, and phosphorus. It rests with the analyst to adopt the one which he finds most practicable in each case.

Carbon and Hydrogen.—The analysis for these elements is that commonly performed for the determination of carbon and hydrogen in organic compounds, that is, combustion of the carbon to carbon dioxide and of the hydrogen to water, the products being collected in suitable absorbents and weighed. The combustion tube may be either of Jena glass or of silica and should be 70-80 cm. long. Its diameter is about 12-14 mm. It is filled as follows, proceeding

from the end at which the air or oxygen used in the combustion enters:—(1) A free space of 5 cm. or more, depending on how far the end of the tube projects from the furnace; (2) a coil of oxidised copper gauze of about 15 cm. length formed by winding copper gauze round a piece of thick copper wire until the roll is of such a size as to closely fit the combustion tube: this prevents the gases diffusing backwards during combustion; (3) a free space large enough to contain the boat in which the coal is burnt; (4) a small plug of ignited asbestos; (5) about 25 cm. of coarse copper oxide, best prepared by cutting copper wire into short pieces, and igniting these in a porcelain basin until thickly coated with oxide; (6) an asbestos plug; (7) about 12 cm. of fused lead chromate: this serves to retain the sulphur dioxide formed by the burning of the sulphur in the coal; (8) an asbestos plug; (9) a free space to the end of the tube. The ends of the tube should project a few centimetres beyond the furnace. They are fitted with rubber stoppers. The stopper at the front or entrance end of the tube is fitted with a short piece of glass tubing through which the air or oxygen used in the combustion enters, and the one at the exit end contains the end of the tube used for the absorption of the water vapour produced in the combustion. Both stoppers should be protected from the heat of the furnace by asbestos shields slipped over the ends of the tube. A good method of preventing condensation of water in the exit end of the tube through its being too cold, and at the same time preventing burning of the stopper by over-

heating, is to enclose the projecting part of the tube between the furnace and the stopper in a rectangular box built of asbestos, and keep the enclosed tube at a temperature of 70° - 80° by means of a microburner at the bottom of the box, the temperature of the tube being indicated by a thermometer which is allowed to hang with the bulb resting on the external wall of the tube. The main part of the tube is heated by a number of burners along its length, which can be raised or lowered at will.

Various types of apparatus may be used for absorption of the water, and carbon dioxide formed. The water is first removed from the exit gases by passing them through a U-tube, fitted with glass stopcocks, and having on the entrance side a bulb in which a large portion of the water can condense. The tube itself is filled with either (1) pumice-stone soaked in concentrated sulphuric acid, or (2) calcium chloride in lumps free from dust, and previously saturated with carbon dioxide by passing a slow stream of the gas through the filled tube for several hours, and thereafter allowing it to remain filled with carbon dioxide overnight. This tube is followed by the carbon-dioxide-absorbing apparatus, which consists either of (1) two Mohr's potash bulbs containing a 50 per cent. potash solution and each having the exit tube connected with a small calcium chloride tube to prevent loss of moisture, or (2) two U-tubes containing soda-lime in lumps and having each the last quarter of the exit limb filled with calcium chloride. The potash should be renewed for each combustion in one of the potash bulbs, the previously

second bulb being then placed first for the next analysis. The soda-lime tubes may be used two or three times until the second one shows more than a slight gain in weight, when they should be refilled. The water-absorption tubes may be used for a considerable number of experiments without renewal. The tubes are connected by short pieces of rubber tubing in such a way that the glass ends meet within the rubber sheaths. The combustion may be carried out entirely in a stream of oxygen, in which case the absorption tubes are weighed both before and after the combustion, filled with oxygen. It may also be started with an air current, and the coke, which it is difficult to burn in air, finally burnt in oxygen, in which case after the combustion is complete a current of air must be passed through the apparatus for such time as may be necessary to displace the oxygen and fill the absorption tubes with air before weighing. The air or oxygen is contained in gas holders over water, and, on its way to the combustion tube, is passed through a purifying tower containing sulphuric acid in the base, then soda lime and calcium chloride in the main part of the tower. This dries the gas and frees it from carbon dioxide. The oxygen should be examined for hydrogen, and, if present, this also must be removed.

To minimise the risk of leakage from the combustion tube, it is a good plan to carry out the combustion under slight suction. This is done by means of a syphon bottle filled with water and placed after the last absorption tube. Just before commencing the combustion when the tube is all fitted up, the

syphon should be started and the tightness of all the connections tested by closing the air or oxygen supply tap and observing if the flow from the syphon completely stops. If it does not do so, some of the stoppers or rubber connections are faulty and must be repaired or replaced. This syphon also serves as a measure of the gas passed through during the combustion if the water delivered by it is caught in a measuring cylinder, and with a little experience one can also determine the rate at which the combustion is proceeding by noting the rate of flow of the water.

The combustion is carried out as follows:—The combustion tube is heated for some time with a current of dry air passing through so as to remove all traces of moisture. While it is cooling, the absorption tubes are weighed, and the coal (·2-·3 gram) also weighed out in a platinum or porcelain boat. The absorption tubes are then attached to the combustion tube and the boat pushed into place in the tube by means of a long wire. The gas holder is then connected up and the whole apparatus tested for tightness, as described above. Air or oxygen, as the case may be, is then allowed to pass through the apparatus at such a rate as to give about one bubble per second through the sulphuric acid in the drying tower, or one drop per second from the syphon tube. The portion of the tube containing the copper oxide is then heated to redness, and that containing the lead chromate to a moderate temperature—400° C. at most. This condition of affairs having been attained, the portion of the tube containing the coal is very

gently heated, great care being taken to avoid driving off the volatile matter too rapidly. The temperature is gradually raised, and finally, when only coke remains, the tube may be heated to bright redness. When nothing but ash remains in the boat the combustion is complete, and the tube is allowed to cool with the air or oxygen passing through. It is advisable in all cases to pass a definite volume of gas through the tube after completion of the combustion (which quantity will depend on the volume of the tube), to ensure that all the products are swept into the absorption tubes. These are then removed, allowed to cool, and weighed. From the gains in weight due to water and carbon dioxide respectively, the percentages of hydrogen and carbon present in the coal are calculated. Instead of the above, the Walker and Blackadder modification of the Dennstedt furnace may be used. In this case the coal is mixed in the tube with powdered copper oxide, instead of being placed in a boat, and the whole combustion is carried out in a current of oxygen.⁷⁹

It should be remembered that if the coal contains carbonates, a high result for organic carbon is obtained. This can be corrected by determining the percentage of carbonate in the coal and making the necessary deduction.

Nitrogen.—This is best determined by means of the Kjeldahl procedure. About 1 gram of the coal is weighed out into a 300 c.c. Kjeldahl flask. 8 grams of pure potassium sulphate, 15-20 c.c. of nitrogen-free concentrated sulphuric acid, and a drop of mercury are added. The potassium sulphate serves to raise

the boiling-point of the sulphuric acid, and the mercury by catalytic action hastens the process of oxidation. The flask mouth is closed by means of a bulb blown from glass tubing, so that the fume from the sulphuric acid is condensed in the neck instead of escaping. The flask is heated gradually until fairly vigorous reaction commences. When the first reaction has slowed down, the contents of the flask are heated further to gentle boiling, and maintained at this temperature until the liquid becomes quite colourless. This generally requires two to four hours. By this means the nitrogen present is all converted into ammonium sulphate. The solution is allowed to cool, carefully diluted with about 100 c.c. distilled water, and transferred to a copper distillation flask which is fitted with a rubber stopper through which passes a tap funnel and a glass tube containing a splash bulb to prevent passage of caustic alkali through splashing, bent twice at right angles, and leading into an upright condenser. The condenser is fitted at its lower end with a tube which passes downwards into an Erlenmeyer flask containing 25 c.c. tenth normal sulphuric acid, into which it dips. Through another hole in the double-bored stopper of the flask passes a bulbed calcium chloride tube filled with glass beads, through which the sulphuric acid has been run into the flask. This prevents the escape of any ammonia not absorbed on bubbling through the sulphuric acid in the flask. When all is connected, about 35 grams of caustic soda dissolved in water are added through the tap funnel, and about 12 c.c. of a concentrated

sodium sulphide solution is also added to precipitate the mercury and so assist in the decomposition of the mercury-ammonium salts usually present. A little granulated zinc is also useful in preventing excessive frothing. The whole is boiled until no more ammonia is expelled, after which the contents of the flask and the beads from the safety tube are transferred to a beaker, and the excess of sulphuric acid titrated with tenth normal caustic soda, using methyl-orange, methyl red, or cochineal as indicator. The percentage of nitrogen in the coal is equal to the number of cubic centimetres of $N/10$ sulphuric acid neutralised multiplied by $\cdot 0014$, divided by the weight of the coal, and multiplied by 100. A blank test should always be carried out on the substances used in the analysis and a corresponding deduction made.

Sulphur may be present in coal (1) as iron pyrites; (2) as sulphates, especially calcium sulphate; and (3) as organic sulphur. The percentage of sulphur in coal is of great importance when the coal is to be used for metallurgical purposes.

The total content of sulphur is usually estimated by Eschka's method.⁸⁰ One gram of coal is intimately mixed in a porcelain crucible with 2 grams of pure magnesium oxide and 1 gram of pure anhydrous sodium carbonate. This is covered with a thin layer of the fusion mixture to prevent any loss on heating. The whole is heated to a dull red heat in a muffle furnace for about two hours. An open bunsen flame is not suitable as a means of heat, as sulphur from the burning gas is sure to contaminate the sample, but, if a muffle is not available, the crucible contents may be

protected from the bunsen gases by the use of an asbestos plate having a hole in the centre in which the crucible is supported. After cooling, the contents are transferred to a beaker and the crucible washed out with distilled water. The volume in the beaker is made up to 100-150 c.c. In order to oxidise any sulphide which may be present, a few drops of bromine water are added. Dilute hydrochloric acid is then added in sufficient quantity to dissolve the carbonates, and, after the effervescence has ceased, the excess of bromine is removed by heating. The insoluble matter of the coal is then filtered off and the sulphate in the boiling filtrate precipitated by means of a 10 per cent. hot barium chloride solution added slowly and with constant stirring. After standing for some hours, the barium sulphate is filtered off, ignited, and weighed, and the percentage sulphur in the coal calculated. A blank experiment on the materials used in the analysis should always be made.

If the sulphur in the ash is estimated by treating the ash from about 4 grams of coal with bromine water and hydrochloric acid, filtering, and precipitating the sulphate as above, the volatile sulphur is obtained by difference. The volatile sulphur can also be estimated directly by burning the coal in a combustion tube in a current of oxygen and leading the gases evolved through hydrochloric acid containing bromine water, and precipitating the sulphuric acid formed as barium sulphate.

The sulphur present as sulphide, sulphate, and organic sulphur can also be separately determined as

follows: ⁸¹—About 5 grams of the coal are treated in a flask with 100 c.c. of hydrochloric acid, the whole being gently boiled for one hour, during which a stream of carbon dioxide is led through the flask, by which means the hydrogen sulphide evolved is led off and passed through a solution of cadmium acetate. This cadmium solution is then treated with 40 c.c. *N*/100 iodine solution, acidified with 1 c.c. of concentrated hydrochloric acid, and the excess of iodine back-titrated with *N*/100 sodium thiosulphate and starch. Each cubic centimetre of *N*/100 iodine used is equivalent to .00032 gram of sulphur present in the coal as sulphide. The solution in the flask which contains the dissolved sulphate is decanted through a filter paper into a beaker, the residue in the flask washed several times with dilute hydrochloric acid, and finally transferred to the filter paper and washed free from acid with distilled water. The solution is neutralised with ammonia and then 20 c.c. of a 10 per cent. hydrochloric acid solution added. The sulphate is then precipitated as barium sulphate in the usual manner. Each gram of barium sulphate is equal to .1374 gram sulphur present in the coal as sulphate. The total sulphur is estimated by Eschka's method, and the difference between the percentage found and the sum of the sulphide and sulphate sulphur gives the percentage of organic sulphur.

Phosphorus.—This is usually present in coal only in small quantity, and its determination is of importance only when the coal is used for metallurgical processes. About 3 grams of the coal are burnt at a moderate temperature. The ash is treated with

concentrated hydrochloric acid and the solution evaporated to dryness on the water-bath and finally on a gently-heated sand-bath. The residue is warmed with a few cubic centimetres of concentrated hydrochloric acid for a few minutes, the acid diluted, and the insoluble silica filtered off. Twenty-five c.c. concentrated nitric acid are added to the filtrate, which is then evaporated almost to dryness to remove the hydrochloric acid. The solution is then diluted and the phosphate estimated gravimetrically by precipitation with ammonium molybdate.

Oxygen.—This can only be determined by difference. The sum of the percentages of carbon, hydrogen, nitrogen, sulphur, and ash is deducted from 100.

IX.

THE ANALYSIS OF COAL—CALORIFIC VALUE.

THE heating value of a coal, or the latent energy residing in it, can be determined in several ways. For instance, the amount of water converted into steam by the combustion of a given weight of coal can be found by means of a "boiler-trial" carried out under specified conditions. If the coal is suitable for the manufacture of producer gas, trials can be conducted in an experimental producer plant, a series of gas analyses being made during the run, and the calorific value of the gas determined by means of a gas calorimeter. The easiest and most direct way, however, of estimating the heating power of a coal is by burning it in a calorimetric bomb in presence of compressed oxygen, and measuring the heat rise produced thereby in a definite weight of water. This method has the additional advantage that only a small quantity of coal is required for the determination.

The bomb consists of a cylindrical vessel of nickel-plated steel with a capacity of about 300 c.c. and supplied with a tightly fitting screw-cover of the same material. This cover is bored with two holes which serve for passing in the oxygen for the combustion and for letting out the products of combustion respectively. These holes can be tightly

closed by means of screw plugs. Through the centre of the cover there passes a platinum wire which is insulated from the cover itself and reaches to about the centre of the bomb. A platinum tube to which is attached a small platinum crucible is also suspended from the lower surface of the lid, and this and the wire both carry little hooks to which the ignition wire used in starting the combustion can be suspended. The lid carries two terminals in contact with these wires. The ignition is caused by means of an iron or thin platinum wire imbedded in the coal, and which can be heated to redness or fused by the short passage of an electric current from accumulators.

The determination is made as follows:—A piece of iron wire of appropriate diameter is weighed, made into a little coil, and incorporated in about one gram of coal by compressing the two in a small briquetting press. The whole is weighed and the weight of the coal found by difference. The briquette is then placed in the platinum crucible and the ends of the iron wire connected with the platinum terminals. The cover is screwed tightly on to the bomb, which is then filled with oxygen at about twenty-five atmospheres' pressure. The whole is placed in a nickel-plated calorimeter vessel containing about 2000 grams of water at room temperature. This vessel containing the bomb is then placed in a double-walled copper vessel which is carefully insulated. The calorimeter vessel is supplied with a thermometer graduated in hundredths of a degree, and which can be read to the nearest thousandth of a degree by means of a lens. The water in this

vessel is kept well stirred by an electro- or water-turbine motor. After the temperature has become equalised between the calorimeter bomb and the surrounding water, the temperature on the thermometer is read ten times at intervals of one minute. During this period the temperature should remain constant within a few thousandths of a degree. The current is then passed through the wire. The wire becomes red-hot and burns along with the coal forming iron oxide. The coal itself is completely burnt to water, carbon dioxide, and sulphuric and nitric acids. The heat evolved is distributed between the material of the bomb and the surrounding water. The thermometer rises rapidly, and readings are taken each minute until the maximum is reached. During the subsequent fall of the thermometer, ten readings are taken at minute intervals, as before the experiment. The bomb is then removed from the water, the pressure released, and the cover unscrewed. Any portion of the iron wire unburnt is weighed, and that weight deducted from the first weighing. For each gram of iron burnt 1600 calories is deducted from the total heat produced.

The nitrogen in the coal is burnt to N_2O_5 , and this dissolves in the water formed to give $2HNO_3$. The heat produced thereby is 1021 calories per gram of nitrogen. The sulphur is burnt to SO_3 , which dissolves in the water to give sulphuric acid. Now, on burning coal in the usual manner, the oxidation proceeds only to the stage of sulphur dioxide, hence the correction to be applied is the difference between the heat formed by formation of H_2SO_4 in solution and that

of gaseous sulphur dioxide. The formation of one gram-molecule of sulphur dioxide from sulphur and oxygen liberates 69,300 calories, and that of one gram-molecule of sulphuric acid in solution from sulphur, oxygen, and water, 141,100 calories. The difference, which represents the conversion of one gram-molecule of sulphur dioxide to sulphuric acid in solution is therefore 71,800 calories.

The quantities of nitric and sulphuric acids formed can be calculated from analysis of the coal for nitrogen and sulphur, or they can be estimated as follows:—The contents of the bomb are transferred to a beaker, and the bomb and cover washed several times with distilled water. The solution is boiled for some time to remove carbon dioxide. The total acidity is then found by titration with $N/10$ baryta solution, using phenolphthalein as indicator. A measured excess of $N/10$ sodium carbonate is then added to precipitate the barium, the precipitate (barium sulphate which is equivalent to the sulphuric acid, and barium carbonate which is equivalent to the nitric acid) is filtered off, well washed, and the solution titrated with $N/10$ hydrochloric acid, using methyl orange as indicator. The excess of sodium carbonate is thus found, and from this the volume of $N/10$ sodium carbonate used in forming barium carbonate, which is equivalent to the nitric acid present. The sulphuric acid is given by the difference between this and the total baryta used. Each cubic centimetre of $N/10$ nitric acid is equivalent to 1.43 calories, and each cubic centimetre of $N/10$ sulphuric acid to 3.6 calories.

A correction has also to be made for loss of heat by radiation. This can be estimated in various ways, and different formulæ are used. A simple form of calculation is that given by Muck⁸²—

If t_1 = the last reading of temperature before the rise
due to combustion

and t_2 = the first reading of temperature after the rise
due to combustion,

d_1 = the average difference of temperature readings
before combustion

and d_2 = the average difference of temperature readings
after combustion, the "cooling constant" of
the apparatus is given by

$$k = \frac{1}{t_2 - t_1} (d_1 + d_2).$$

The mean temperature at the circumference of the calorimeter during combustion is calculated by the formula:—

$$T = \frac{d_2 t_1 + d_1 t_2}{d_1 + d_2}.$$

The difference between this value and the thermometer readings during the combustion are plotted on squared paper, and the areas (A_1 and A_2) below and above the line of mean temperature estimated, and the correction is then given by the formula—

Correction = $k(A_2 - A_1)$. See example on page 83.

Only a part of the heat produced by the combustion is taken up by the water in the calorimeter, part being also absorbed by the bomb, the stirrer, the containing-vessel, and the thermometer. It is therefore necessary to determine the heat-value of the

apparatus. This value is calculated for the heat taken up by the apparatus for one degree of temperature rise in the calorimeter water, and the heat capacity thus found translated into an equivalent amount of water. It is best determined by burning in the bomb a known weight of a substance such as cane-sugar or benzoic acid, whose calorific value is accurately known, and finding the difference between the value given by the rise in temperature shown by the thermometer and the true value.

Example—

Weight of benzoic acid	=	0.7300	grams.
„ iron ignition wire	=	0.0160	„
„ water in calorimeter	=	2000	„

Observed rise of temperature = 1.813°

Correction for radiation = $.012^{\circ}$

Corrected rise of temperature = 1.801°

Calculated heat of combustion of benzoic acid
(6333 cal. per gram) = 4620.9 cal.

Calculated heat of combustion of iron		
wire	(1600 cal. per gram)	= 25.6 „
Total		= 4646.5 „

\therefore Calculated heat for 1° temperature rise = 2580 cal.

Heat absorbed by water = 2000 „

\therefore Equivalent of calorimeter = 580 grams
of water.

In order to obtain a value for the heat production which will correspond to the practical application of the coal the fact must be noted that in ordinary combustion in furnaces, etc., the water vapour formed is not condensed. This water vapour is produced

from (1) the moisture content. (M) of the coal, and (2) the hydrogen (H) in the coal. The total is therefore $M + 9H$. This water is condensed in the bomb and heat is thereby liberated. The technical heat value therefore differs from the calorific value by this amount. Since 1 gram of water on condensing liberates 600 calories, the heat value is equal to the calorific value, less 6 ($M + 9H$).

An example of the method of calculating the calorific value of a coal may be given in order to show how all the above corrections are estimated and applied.

Example—

	Weight of iron wire for ignition	= 0.0152 grams.
	Weight of iron wire + coal	= 1.0325 „
∴	Weight of coal	= 1.0173 „
	Weight of water in calorimeter	= 2026 grams.
	Water equivalent of bomb, etc.	= 315 „
	Total	= 2341 „

Readings of thermometer before combustion:—

Time in Minutes.	Reading.	Difference.
0	15.233	...
1	15.237	.004
2	15.241	.004
3	15.244	.003
4	15.248	.004
5	15.253	.005
6	15.257	.004
7	15.262	.005
8	15.267	.005
9	(t_1) 15.271	.004

Average = .0042 (d_1).

Readings of thermometer during rise due to combustion :—

Time in Minutes.	Reading.
0	15·271
1	15·635
2	17·603
3	18·435
4	18·617
5	18·634

Readings of thermometer after combustion :—

Time in Minutes.	Reading.	Difference.
0	(t_2) 18·634	...
1	18·630	·004
2	18·625	·005
3	18·620	·005
4	18·615	·005
5	18·610	·005
6	18·606	·004
7	18·602	·004
8	18·598	·004
9	18·594	·004

Average = ·0044 (d_2).

Correction for radiation :—

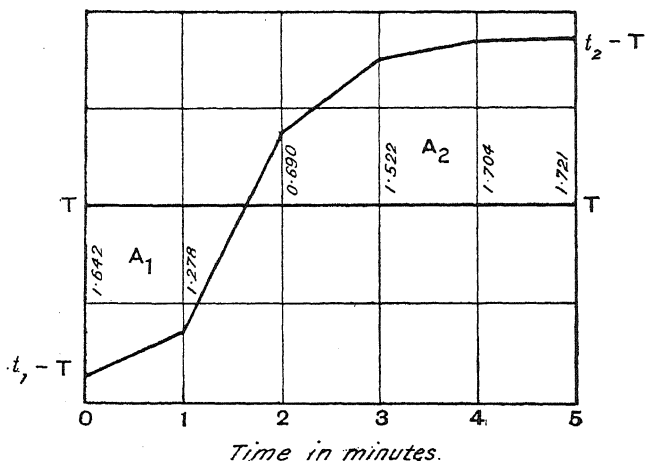
Estimated mean temperature (T) of outside of calorimeter

$$= \frac{d_2 t_1 + d_1 t_2}{d_1 + d_2} = 16·913.$$

“Cooling constant” (k) of apparatus

$$= \frac{1}{t_2 - t_1} (d_1 + d_2) = ·0026.$$

The graph showing the differences between T and the temperatures during thermometer rise is:—



The area $A_1 = 1.9$

$A_2 = 4.5$

$A_2 - A_1 = 2.6$

\therefore correction for radiation $= k(A_2 - A_1) = .007^\circ$.

Correction for water condensation—

Analysis of the coal gave

Moisture = 1.20 per cent. (M)

Hydrogen = 4.02 „ (H)

\therefore correction for 1 gram coal $= 6(M + 9H) = 224$ cals.

Correction for nitric acid and sulphuric acid formed—

N/10 Baryta used = 8.5 c.c.

N/10 sodium carbonate added = 2.8 „

N/10 hydrochloric acid for back-titration = 1.3 „

∴ N/10 alkali used for nitric acid	= 1.5 c.c.
N/10 alkali used for sulphuric acid	= 7.0 „
∴ correction for nitric acid = 1.5×1.43	= 2.1 cal.
correction for sulphuric acid = 7.0×3.6	= 25.2 „

Reading of thermometer at beginning of combustion	= 15.271°
Reading of thermometer at end of rise	= 18.634°
Difference	= 3.363°
Correction for radiation	= 0.007°
	<u>3.370°</u>

∴ heat produced = 3.370×2341	= 7889.2 cal.
Deduction for iron wire (0.0152×1600)	= 24.3 „
„ nitric acid formed	= 2.1 „
„ sulphuric acid formed	= 25.2 „
Nett heat	= <u>7837.6</u> „
∴ heat evolved by 1 gram coal	= 7704 cal.
Deduction for water condensation	= 224 „
Final value	= <u>7480</u> „

X.

THE PROPERTIES OF COAL ON COMBUSTION.

It is of great interest to the user of coal to know what deductions he can draw from the analysis of a coal as to its properties on combustion. For instance, the questions of fusibility or of coke formation, or of the character of the flame produced, are of great importance in many industries. Is it possible to deduce these from analytical results? Many attempts have been made to prepare a classification of coals as to these properties from their analyses. In most cases these have failed because of the fact that the properties of a coal depend not so much upon the percentage constituents as found by proximate or ultimate analysis as on the presence or absence in the coal of certain compounds of carbon of very definite natures. Nevertheless, certain general deductions are possible, although these cannot always be considered as infallible.

Von Richters⁸³ states that the larger the percentage of oxygen in a coal, the larger is the moisture content and the quantity of volatile matter, and therefore the smaller the yield of coke.

The porosity of the coke formed depends to a large extent on the fusibility of the coal. Difficultly fusible coals are very viscous on heating, and the

gases evolved cannot escape easily but blow up the coal mass into small bubbles. When these burst the walls do not fall together again, and the coke is thus rendered porous. With easily fusible coals, the gases escape at once, and the easily flowing cell walls come together again, thus forming a dense coke. It is also apparent that the lower the temperature of coking, the more viscous is the coal, and therefore the more porous the coke formed. Donath⁸⁴ thus describes the process of coke formation:—"At a relatively low temperature, a mixture is formed of the perfectly fusible constituents, which consist of the decomposition products of the resinous and fatty parts of the coal-forming material, as well as certain substances which produce the pitch formed on destructive distillation. These substances decompose early in the heating without leaving behind any coaly residue. The products thus formed act on the cellulosic parts of the coal and the parts formed from proteins, cementing them, as it were, into one carbonaceous compound or into a more homogeneous mixture. At a higher temperature the protein derivatives soften, whereby the whole is again further cemented together, and yield on decomposition at a still higher temperature the more refractory sulphur- and nitrogen-containing constituents which are recognisable in all cokes."

Properties of the Flame.—The properties of the flame evolved on burning coal depend to a great extent on the percentage composition of the coal. The coking test made in proximate analysis gives considerable clue as to the nature of the coal. Coals

containing much volatile matter, or which are rich in hydrogen, give off a gas which ignites readily on escape from the crucible, burning with a long, steady, luminous, and sooty flame. The gases from coals having little volatile matter, or poor in hydrogen, ignite less readily, are evolved more slowly, and produce a short, less luminous, and only slightly sooty flame. Coals with very little volatile matter, or very poor in hydrogen, such as many anthracites, give off gases which burn with a practically colourless, short flame, and are more or less inodorous.

Effect of Ash in Coals.—Coals which contain much ash usually give a sooty-black coke which is lustreless, and, except when the hydrogen percentage is high, a flame which, although at first it may be brightly luminous, very soon becomes small in size, only slightly luminous, but persistent. The cause of the lack of lustre in the coke is that the high percentage of ash prevents a general melting of the coal during combustion.⁸⁵ That the percentage of the coal remaining as coke depends to some extent on the ash present has been shown by Muck.⁸⁶ Using a coal with 3·7 per cent. ash and mixing it with different percentages of highly powdered quartz, he showed that, on igniting in a platinum crucible, the coke left increased with the percentage of quartz present. The following are some of his figures—

						Coke (reckoned on quartz-free coal). Per cent.
1.	Coal with admixture of 30	per cent.	quartz			74·88
2.	„	„	50	„	„	76·22
3.	„	„	60	„	„	79·31

The nature of the cokes also varied, for while all were slightly swollen and bore "bud-like" excrescences, No. 1 was compact, well-caked, and having the lustre of graphite; No. 2 was more friable, sooty-black, and almost lustreless; and No. 3 very friable and entirely lustreless. It should be remarked that in general the ash-forming material in coals is not a substance like quartz, which is unaltered on heating, but more frequently consists of compounds which lose weight on ignition, such as hydrated silicates which give off water, or carbonates which give off carbon dioxide. If these are present in any quantity a considerable error may be introduced into the calculation of the percentage of volatile matter, which is estimated by difference in the proximate analysis. It is not possible to avoid this as the pure coal substance cannot be separated, but it should always be borne in mind in considering analytical data.

Caking Qualities of Coal.—The property of "caking" or of forming a non-friable coke is of great importance in industrial practice. The method of finding a "caking-value" adopted first by Campredon⁸⁷ is still much used. Several mixtures of the coal are made with different percentages of pure fine sand. These are coked in a platinum or porcelain crucible, and the maximum percentage of sand determined with which the coal will still form a consistent coke. This method has the objection that in many cases the natural ash of the coal contains compounds capable of forming silicates with the sand, thus entirely altering the properties of the ash. Dunn⁸⁸ proposes using a good anthracite, of which

the ash is indifferent to that of the coal tested, in place of the sand used by Campredon.

Conclusion.—It will be seen from the above statements that the qualities of a coal cannot at once be determined from its proximate or ultimate analysis, although in most cases these afford valuable information on the subject. In general, special tests must be made which have reference to the uses to which the coal is to be put. It is not infrequently the case that a coal, which from its analysis would appear to be perfectly suitable for a certain object, is altogether useless because of some more or less insignificant point which is not demonstrated by the usual routine tests, and, on the other hand, an apparently useless coal may contain some hidden property which makes it eminently valuable.

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